# United States Court of Appeals for the Second Circuit



**EXHIBITS** 

# 74-1765

13

# United States Court of Appeals

FOR THE SECOND CIRCUIT
Appeal No. 74-1765

Esso Research and Engineering Company,

Plaintiff-Appellant,

V.

KAHN AND COMPANY, INC. and CHANDLER-EVANS, INC.,

Defendants-Appellees.

ON APPEAL FROM THE UNITED STATES DISTRICT COURT FOR THE DISTRICT OF CONNECTICUT

# PLAINTIFF'S AND DEFENDANTS' EXHIBITS

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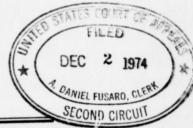
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FOR THE SECOND CIRCUIT
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v.

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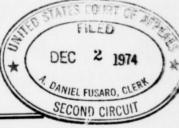
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### PLAINTIFF'S EXHIBIT 1

Skarstrom U.S. Patent No. 2,944,627



C. W. SKARSTROM
METHOD AND APPARATUS FOR FRACTIONATING
GASEOUS MIXTURES BY ADSORPTION

2,944,627

Filed Feb. 12, 1958

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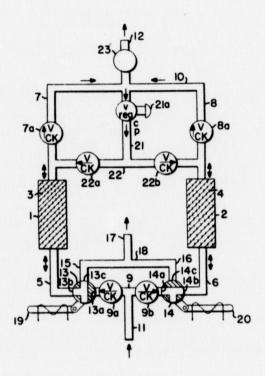


FIG.-I

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Inventor

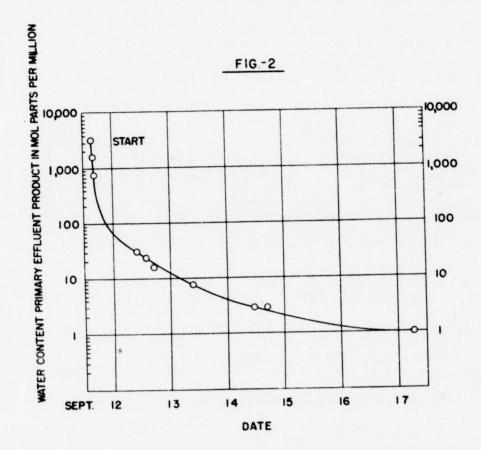
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METHOD AND APPARATUS FOR FRACTIONATING
GASEOUS MIXTURES BY ADSORPTION

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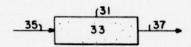


FIG.-3

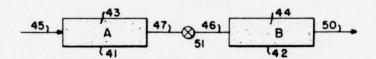


FIG.-3A

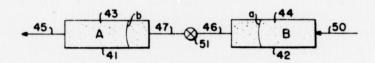


FIG. - 3B

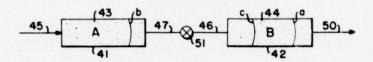


FIG. - 3C

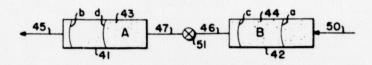


FIG. - 3D

Charles W. Skarstrom Inventor

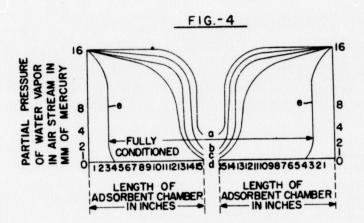
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Charles W. Skarstrom

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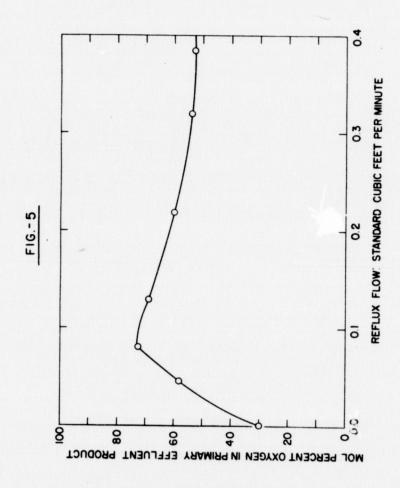
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2,944,627

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Charles W. Skarstrom Inventor

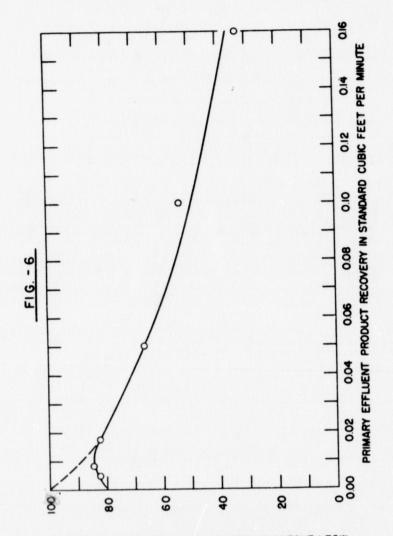
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C. W. SKARSTROM
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GASEOUS MIXTURES BY ADSORPTION

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MOL PERCENT OXYGEN IN PRIMARY EFFLUENT PRODUCT

Charles W. Skarstrom Inventor

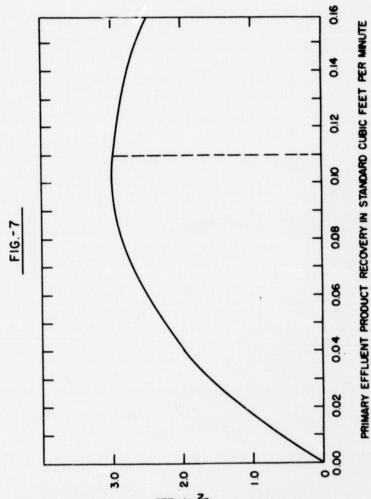
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GASEOUS MIXTURES BY ADSORPTION

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(VOLUME TOTAL PRIMARY EFFLUENT PRODUCT-VOLUME REFLUX FLOW) X (PERCENT  $o_{\rm S}$  IN PRIMARY EFFLUENT PRODUCT-PERCENT  $o_{\rm S}$  IN FEED

Charles W. Skarstrom

Inventor

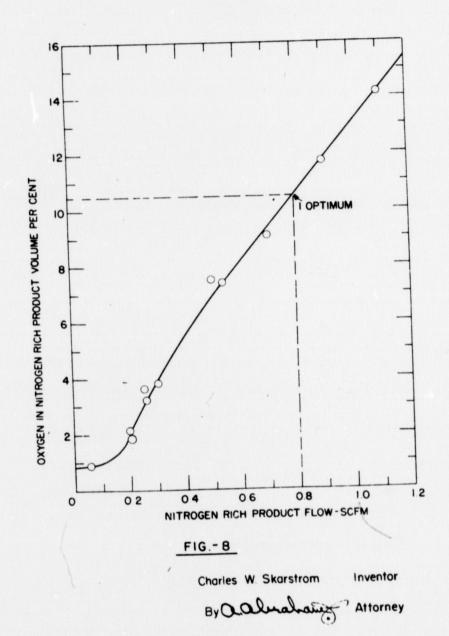
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C. W. SKARSTROM
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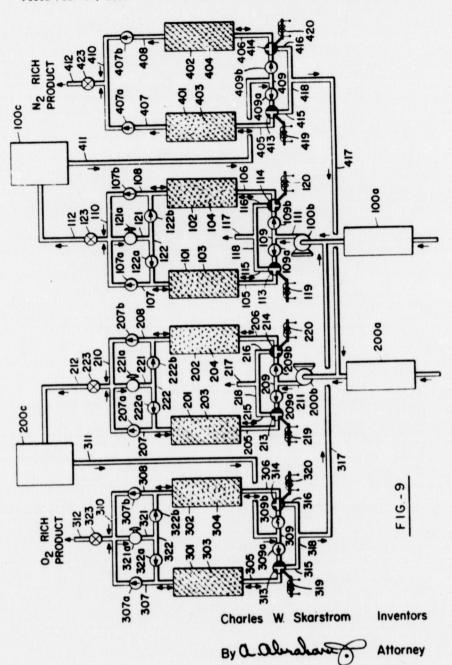


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C. W. SKARSTROM
METHOD AND APPARATUS FOR FRACTIONATING
GASEOUS MIXTURES BY ADSORPTION

Filed Feb. 12, 1958

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#### 2,944,627

METHOD AND APPARATUS FOR FRACTIONAT-ING GASEOUS MIXTURES BY ADSORPTION

harles W. Skarstrom, Montvule, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Filed Feb. 12, 1958, Ser. No. 714,780 36 Claims. (Cl. 183-4.7)

This invention relates to a method and apparatus for 15 fractionating gaseous mixtures. The invention relates, more particularly, to a method and apparatus for removing one or more key components from a gaseous mixture or gas stream containing such components. The invention further relates to such a method and apparatus 20 as employed for the separation from a gaseous mixture of one or more component contaminants. The invention also relates to a method and apparatus employed for the purpose of producing an efficient product wherein by removal of one or more components of the original mixture, the percentage concentration of more desirable components is increased in the resulting product. One specific adaptation of the invention relates to the drying of a gaseous mixture, such as air, by removal of water vapor. Also with specific reference, the invention relates to a method and apparatus whereby nitrogen is removed from a stream of atmospheric air to increase the concentration of oxygen in the effluent product stream. In addition, the invention relates to a method and apparatus whereby oxygen is removed from a stream of atmospheric air to increase the concentration of nitrogen in the effluent product stream. In this connection, the invention particularly relates to a combined system for separating air into its major components of oxygen and nitrogen, employing the fractionation method and apparatus herein disclosed.

The present application is a continuation-in-part of an application Serial No. 670,342, filed in the United States Patent Office under date of July 5, 1957, now aban-

In various industrial processes, moisture-free or oxygen- or nitrogen-rich air streams are essential to proper operating procedures. Many methods and a variation of apparatus combinations are known or have been proposed to obtain such ends. Most involve either complicated procedures or equipment expensive to assemble and operate. It is an object of the present invention to provide a simple method and apparatus which, with minor modification, may be employed in a multitude of situations where the purification or concentration of

gaseous mixtures is desired. Specifically, the objects of the present invention may be stated as follows:

(1) To provide a separation system such as an adsorption system or diffusion system for the drying of air or other gaseous materials, without need for employment of extraneous heat to restore the adsorbent used in the system

(2) To provide such a system, wherein relatively small amounts of adsorbent material are required for efficient operation, and therefore, wherein expenditures for equipment are considerably reduced.

(3) To provide a method and apparatus whereby oxygen and/or nitrogen-rich products may be recovered pensive or complicated procedures

(4) To provide a method and apparatus whereby a

gaseous mixture may be fractionated to provide a series of effluent product streams in which each such effluent stream is rich in at least one component portion of the gas mixture supplied to the system as a feed material.

The terms "gas" and "gaseous" as employed in the following description or claims are intended to include not only materials that are conventionally considered to be gases, but also those materials conventionally considered to be vapors. Also, the term "key component" as employed in the following description or claims is used to designate the component or components selectively adsorbed from a stream of a gaseous material initially fed to the system.

The invention and its objects may be more fully understood from the following description when it is read in conjunction with, and with refreence to the accompanying drawings in which:

Fig. 1 is a diagrammatic showing of an apparatus according to the present invention, illustrating flow connections and controls adapted to accomplish the method contemplated;

Fig. 2 illustrates graphically an operation in which a system according to the present invention was employed to remove moisture from atmospheric air, and showing progressive conditioning of such a system to produce a substantially constant output of air dried from an initial moisture content of 4000 mol parts per million to approximately 1 mol part per million;
Figs. 3 to 3D inclusive schematically illustrate the

fundamental operational concepts involved in the practice of the present invention;

Fig. 4 is a graphic illustration of the manner in which the conditioning of a system according to the present invention proceeds to produce a result substantially as illustrated in Fig. 2;

Fig. 5 is a graphic illustration of the results obtained by an operation according to the present invention. wherein the system was employed for the purpose of removing nitrogen from an input air stream to produce an oxygen-rich effluent product, and specifically indicating the effect of modifying one operating condition while maintaining another constant;

Fig. 6 illustrates graphically the effect produced by reversing the roles of the modified and constant operating conditions in the operation represented by Fig. 5;

Fig. 7 illustrates graphically the determination of an optimum result from a system operating under the conditions represented by the showing of Fig. 6, wherein the volumetric recovery of a product effluent is related to the percentage oxygen enrichment of such effluent;

Fig. 8 illustrates graphically the determination of an optimum result from a system adapted to concentrate nitrogen in the primary effluent product derived from a gaseous mixture, wherein nitrogen is a major com-

ponent portion; and
Fig. 9 is a diagrammatic showing of a system for
fractionating a gaseous mixture of at least two major components to produce separate effluent product streams, each rich in one such major component.

In the apparatus as shown by Fig. 1, the numerals 1 and 2 each designates one of a pair of adsorber vessels. Each vessel is adapted to contain and be substantially fully packed with an adsorbent material, to be later described in greater detail. As shown, the adsorbent packing material in vessel 1 is designated by the numeral 3, and that in vessel 2 by the numeral 4.

Each vessel is equipped with conduit connections providing for the passage of untreated or treated gaseous from atmospheric air without liquefaction or other exwise handling such materials in the system. The numerals 5 and 6 respectively designate combined input and purge 2,944,627

conduits for the respective vessels 1 and 2, and the numerals 7 and 8 correspondingly designate primary effluent discharge conduits. Each of the conduits 5 and 6 is connected at its outer end to a common inlet manifold conduit 9, and each of the conduits 7 and 8 are in turn connected to a common discharge manifold conduit 10. A conduit 11 for introducing an initial gaseous material feed into the system is connected to the inlet manifold 9, while a conduit 12 connects with the discharge manifold 10 to provide for discharge of a first product effluent 10 from the system.

The numerals 13 and 14 designate respective elements of a pair of three-port, flow-switching valves connected in the manifold 9 on opposite sides of the connection thereto of the feed or supply conduit 11, and respectively intermediate such connection and the conduits 5 and Check valves 9a and 9b are also disposed in the manifold between the supply conduit connection thereto and the respective valves 13 and 14. These check valves are adapted to permit flow only in the direction of the valves 13 and 14 respectively. In the respective valves 13 and 14, the ports are designated by the letters a, b, and c plus the numeral designating the valve. In each valve the port a is connected to that portion of the manifold 9 communicating directly with the supply conduit 11; the port b is connected to that portion of the manifold communicating directly with a corresponding input and purge conduit such as 5 or 6; and the port c is connected to a conduit for discharge of a second effluent from one of the adsorber vessels. As shown, the ports 13a and 14a are connected to communicate through manifold 9 with supply conduit 11; ports 13b and 14b are connected to communicate through manifold 9 with conduits 5 and 6 respectively; and the ports 13c and 14c are connected to discharge conduits 15 and 16 respectively for discharge of a secondary effluent from the respective vessels 1 and 2. The conduits 15 and 16 in turn communicate with a common discharge conduit 17 through a manifold connection 18

The valves 13 and 14 are preferably provided for auto- 40 matic, cyclical operation so as alternately to connect one of the vessels 1 and 2, through their respective conduit connections 5 and 6 and manifold 9, with either the supply conduit 11 or an effluent discharge conduit con-nection 15 and 16 respectively. In the drawing, the valves 13 and 14 are representatively equipped for auto-matic operation as by means of solenoids 19 and 20 respectively. Also, as thus equipped, the solenoids 19 and 20 are preferably activated by means such as a cycle timing device, not shown.

In the apparatus illustrated, the valve 13 has been actuated to provide for purge discharge from the vessel 1 through conduits 5, 9, and 15 by way of valve ports 13b and 13c. At the same time, or slightly in advance, the valve 14 has been actuated to provide for introduction of a gaseous feed material into the vessel 2 through conduits 11, 9 and 6 by way of the valve ports 14a and 14b. Subsequent operation of the valves in a regular cycle, as later described, would accomplish an opposite relationship of the valves to their respective conduits and communicating vessels.

Now referring further to the conduit connections which include the conduits 7 and 8 and manifold 10, as shown, the latter is provided with a branch conduit con 21 in which is disposed a pressure reducing control valve 21a. This valve may be differential control valve designed to maintain a relatively constant pressure differential between the inlet and the outlet ports thereof. Additionally, and as particularly illustrated in Fig. 1, valve 21a may exercise control to maintain a constant pressure at its outlet port. Flow through the valve is always 70 in the direction indicated by the arrows.

The numeral 22 designates a conduit cross section between the conduits 7 and 8, which cross connection 22 includes check valves 22a and 22b adapted to close against flow from and to open for flow toward the re-

spective conduits 7 and 8. Check valves 7a and 8a respectively provide against flow through the conduits 7 and in the direction of the respective vessels 1 and 2 with which these conduits communicate.

Reverting now to the adsorbent packing material designated in the vessels 1 and 2 by the numerals 3 and 4 respectively, this material may be any adsorbent material which has a selective affinity for one or more of the components of the gas mixture supplied to the system by way of the conduit 11. As shown, the adsorbent material is uniform and continuous throughout each vessel. If desired, however, the vessels may be packed with a number of different adsorbent materials arranged in layers. In such instance, it is preferred that the layers be physically separated. For example, separator plates may be introduced to extend diametrically across the vessel, or each adsorbent may be prepacked in a suitable carrier container and the several containers inserted to form a series from one end of a vessel to the other.

Depending upon the operation contemplated, the ad-sorbent employed may be selected from such materials as activated carbon, alumina, silica gel, glass wool, adsorbent cotton, and even soft tissue paper. Various metal oxides, clays, Fuller's earth, bone char, etc. also have adsorbent characteristics which may be utilized according to the present invention. Still another adsorbent material of the character contemplated is one known as Mobil-Deads, which is a siliceous moisture adsorbing compound.

Other absorbent materials suitable for employment ac-

cording to the present invention include materials known as molecular sieves. This class of materials includes certain zeolites, both naturally-occurring and synthetic, which have crystalline structures containing a large number of small cavities interconnected by a number of still smaller holes or pores, the latter being of exceptional uniform size. The pores may vary in diameter from 3 to 5 Angstrom units, to 12 to 15 or more. For a particular molecular sieve material, however, the pore sizes are substantially uniform and accordingly the material normally will be designated by the characteristic size of its pores.

The scientific and patent literature contains numerous references to the adsorbing action of natural and synthetic zeolites. Among the natural zeolites having this sieve property may be mentioned chabasites and analcite. colite with molecular sieve properties is described in U.S. 2,442,191. Zeolites vary somewhat in composition, but generally contain silica, aluminum, oxygen, and an alkali and/or alkaline earth element, e.g., sodium and /or calcium, magnesium, etc. Analcite has the empirical formula NaAlSi<sub>2</sub>O<sub>6</sub>.H<sub>2</sub>O. Barrer (U.S. 2,306,610) teaches that all or part of the sodium is replaceable by calcium to yield, on dehydration, a molecular placease by careful to yield, on denyation, a molecular sieve having the formula (CaNa<sub>2</sub>) Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>.2H<sub>2</sub>O. Black (U.S. 2,522,426) describes a synthetic molecular sieve having the formula 4CaO.Al<sub>2</sub>O<sub>2</sub>.4SiO<sub>2</sub>.

The synthesis of molecular sieves having uniform

pore sizes of 4 and 5 Angstrom units may be accomplished by mixing an aqueous solution of an alkali metal silicate having a ratio of alkali metal oxide/SiO<sub>2</sub> of about 0.8 to 1 or higher with a solution of sodium aluminate 0.8 to 1 or higher with a solution or sodium aluminate having a ratio of Na<sub>2</sub>O to Al<sub>2</sub>O<sub>2</sub> of about 1/1-3/1 at a temperature of from about 160° to about 215° in such proportions as to give a ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>2</sub> in the mixture of 0.5-3/1. The mixture is held at the stated temperatures for a period of time sufficient to form a crystalline sodium aluminosilicate, which is a molecular sieve material having a uniform pore size of about 4 Angstrom units. A pore size of about 5 Angstrom units may be produced in this material by base exchange reaction with an alkaline earth metal such as calcium, in the form of calcium chloride for example. In either instance, the molecular sieve material produced is water washed and activated by calcining.

having a ratio of alkali metal oxide/SiO<sub>2</sub> of about 1/1 or higher with a solution of sodium aluminate having a ratio of Na2O to Al2O3 of 1/1-3/1 at 160° to about 250° F. in proportions such as to give a ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> in the mixture of 3/1-10/1. This mixture is then held at the stated temperatures for at least an hour, and preferably longer, thereby producing the molecular sieve material desired. The recovered sieve material is

water washed and activated by calcining. A large number of other naturally-occurring zeolites 10 have molecular sieve activity, i.e., the ability to selectively adsorb certain components or component portions of a gaseous mixture. This selectivity stems from the fact that only molecules small enough to enter the pores will be adsorbed. Molecule size alone, however, is not 15 the sole requirement for selective adsorption. It appears that a relative affinity of a molecule for the adsorbent as compared to other molecules or an initial relative rate of adsorption phenomena must be present. Of the materials contemplated for use according to the present in-vention, one having a uniform pore size of about 4 Angstroms has been found especially suitable for concentration of nitrogen in a primary effluent product derived from atmospheric air. A molecular sieve material having a uniform pore size of about 5 Angstroms has 25 been found to be a satisfactory adsorbent for the concentration of oxygen in the primary effluent product derived from atmospheric air, according to the present invention. When employed in substantially the same manner as the 5 Angstrom pore size molecular sieve material, a molecular sieve material having a uniform pore size of about 13 Angstroms also has been found to be suitable for the concentration of oxygen in the primary effluent product derived from atmospheric air. Each of the molecular sieve materials mentioned also 35 exhibits an affinity for moisture, and to some extent carbon dioxide. Accordingly, the primary effluent product derived by the use of these materials from a feed stream of atmospheric air will not only be rich in either nitrogen or oxygen, according to the material used, but

also will be dry.

The 4 A., 5 A., and 13 A. molecular sieve materials have certain characteristic affinities for particular types of hydrocarbons. In this respect, the adsorptive characteristic of 4 A., 5 A., and 13 A., molecular sieves are 45

represented in the following table:

only slight affinity for carbon dioxide. Preferably the adsorbent material employed is one which has an affinity for those components not desired in a primary effluent product, or which may be most advantageously recoverable from a secondary effluent product, both as later identified.

In the preferred practice of the method, according to the present invention, a stream of a gaseous mixture under positive pressure is passed, cyclically and in alternating sequence, through each of two paired adsorption zones, the ambient atmosphere of the zones being substantially maintained at a temperature such as to maintain the feed material and the effluent products in a vapor or gas phase. The stream introduced into each zone is sed over and through a body of an adsorbent contained in the zone, which adsorbent material has a selective affinity for at least one key component portion of the mixture. During passage of the original feed stream of the mixture through a zone, the zone is on an adsorption cycle. During this cycle, the zone is maintained at substantially the pressure of the original feed stream introduced thereinto. After passage through the zone, a gaseous effluent product is discharged from the zone under substantially the pressure of the initial stream.

While either zone is on an adsorption cycle, pressure on the other zone of the pair is reduced, as by opening it to the atmosphere or another zone of reduced pressure. In this condition, the other zone is on a desorption cycle. At substantially the same time, a portion of the primary effluent product from the zone then on an adsorption cycle is withdrawn from the total primary effluent discharge, and this withdrawn portion is introduced into the reduced pressure zone, which is on a desorption cycle, so as to pass over and through the body of the adsorbent contained therein. Passage of this withdrawn portion through the zone on desorption cycle is in counterflow relation to passage of the initial stream passed through such zone while it was on adsorption cycle. As thus introduced, the discharged primary ef-40 fluent product is relatively free of the key component or components retained by and present in the adsorbent contained in the zone on a desorption cycle. Also the adsorbent therein will have been slightly heated by the heat of adsorption induced during a previous adsorption cycle. By proper adjustment of the adsorption-desorption cycle periods, the heat of adsorption during the

Adsorbed on 4 A. and 5 A.	Adsorbed on 5 A. but not 4 A.	Not adsorbed on 4 A. or 5 A.	Adsorbed on 13 A.
(1) Ethane.	(1) Propane and higher n- paraffins.	(1) Isoparaffins.	(1) All hydrocarbons within gasoline boiling range.
(2) Ethylene.	(2) Butene and higher n- olefins.	(2) Aromatics.	(2) Aromatics strongly ad- sorbed.
(3) Propylene.	orans.	(3) All cyclics with 4 or more atoms in ring.	(3) Diolefins strongly adsorbed.

As indicated from this table the method and apparatus according to the present invention may be employed for the separation of materials such as ethane, ethylene, or propylene from a mixture with propane and higher nparaffins or butene and higher n-olefins by the use of 4 A. sieves. Likewise, isoparaffins, aromatics and all cyclics with 4 or more atoms in the ring may be separated from any of the previously mentioned hydrocar-bon material by the use of either 4 A. or 5 A. molecular

As has been indicated above, many of the adsorbent materials listed are selective for more than a single key component. For example, activated alumina may be employed to adsorb water vapor and carbon dioxide simultaneously from a gaseous mixture in which they may be present, while silica gel adsorbents, including Mobilbeads, although adsorbent for water vapor, have pressure cycle is conserved and available to counteract the effects of cooling produced during the desorption

One great advantage of the present process is the conservation of heat evolved on the adsorption cycle. esses as heretofore known in the art conducted the adsorption cycle for a period sufficient to raise the delta T appreciably, thereby permitting or causing heat to flow through the bed, as well as through the walls of the adsorption vessel, thus to be substantially lost. In accordance with the present invention, wherein rapid cycling is employed between the adsorption and the desorption phases, the delta T on the adsorption zone is relatively small. This tends to greatly reduce the flow of heat. Due to the short time on the adsorption cycle, heat will not have time to flow through the hed, and through the walls of the vessel into the surrounding at-

mosphere. By rapid cycling from adsorption to desorption in the respective zones, the desorption cycle will substantially completely utilize the heat produced during the adsorption cycle. As pointed out above, this is due to the low delta T attained, and due to the lack of time for dissipation of the heat of adsorption. In effect, the beds function as highly efficient, rapidly cycled, bead heat exchangers. Generally, the time on the adsorption cycle in accordance with the present invention does not exceed 2-3 minutes and is preferably less than 1 minute. A very 10 desirable time on the adsorption cycle is less than 20 seconds as, for example, 10 seconds. The particular times utilized depend upon various factors, such as the particular adsorbent utilized, the height of the bed, the nature of the key component, and other operating vari- 15

The combination of temperature and reduced pressure, plus the flushing or scavenging effect of the primary effluent product reflux portion used for backwashing, prepares the adsorbent to adsorb the key component or 20 components from the stream of the gaseous mixture introduced during the next adsorption cycle for this zone Desorption of the adsorbed key component is additionally facilitated by the fact that the gaseous mixture constituting the primary effluent product reflux portion which is passed through the zone has acquired a renewed capacity to take up the key component desorbed from the adsorbent. In effect, the desorption step, accomplished in one zone of a pair of zones, involves a backwashing action by the primary effluent product reflux portion withdrawn from the primary product stream discharged from the contemporary adsorption cycle of the other zone in such pair, and may be accomplished without addition of heat from an outside source.

For the purpose of this description, the effluent discharged from a zone which is on its adsorption cycle is termed the "primary effluent product," while the ef-fluent discharged from a zone which is on its desorption cycle is termed the "secondary" effluent product. In the primary effluent product, the key component or components will be present in a minimum concentration. In the secondary effluent product, the key component or components will be present in a maximum concentration.

As a result of the backwashing step for desorption of the key component or components from the adsorption zones, to a degree, the components of the secondary effluent product will correspond to those of the initial feed of the gaseous mixture. The primary effluent product normally will be the product toward which the method is directed. Where the secondary effluent product has no specific utility, as where the adsorbed key components may be such as water vapor and small amounts of car-bon dioxide, during its desorption cycle, the discharge from either zone may be vented to the atmosphere, or otherwise disposed of as a waste product. Where the secondary effluent may be such as to warrant recovery of the adsorbed key components, it may be discharged to an accumulator or storage zone, or fed to a suitable recovery or treating zone directly, in any suitable fashion.

In the method contemplated, the initial gaseous mixture fed to the system should be a material which does not contain appreciable amounts of components which exhibit higher heats of condensation or adsorption than the key components, under the operation conditions presently contemplated by this invention, and which are also strongly adsorbed by the adsorbents selective for such key components. Where components which have such characteristics are present in appreciable amounts, their adsorption tends unduly to raise the temperature of the adsorbing zone, and thereby to increase the vapor pres- 70 sure of an adsorbed key component beyond the condition at which it may be satisfactorily retained or accepted by the adsorbent. Likewise, under such conditions, desorption of the components having those undesirable characteristics set forth above, tend unduly to lower the 75

temperature of the desorbing zone beyond the condition at which the key component is readily given up by the adsorbent. To some extent, however, the effect of such strongly adsorbed components may be counteracted by provision of heat exchange means in the respective adsorption zones whereby the temperatures of the zones may be maintained at levels such as to permit effective adsorption and desorption of the key components. For example, the heat produced in an adsorption cycle in one zone may be utilized to counteract the cooling effect produced by the desorption cycle in the other zone.

The apparatus of the present invention, as illustrated by Fig. 1, has particular utility in a method, such as nerally described above, for drying air streams. such employment, a cycle timer (not shown) was electrically connected to activate the solenoids 19 and 20, and thereby to actuate the valves 13 and 14 at three minute intervals; each valve being "open" for such period while the other was "closed" for that period. When "open" a valve provides for communication

between the inlet conduit 11 and one of the adsorbers by way of the valve and the connecting conduits. In the drawing, the valve 14 is "open" and provides such com-munication by way of ports 14a and 14b, and the conduit 6 to adsorber 2. The other valve 13 is shown as "closed," in which position it provides communication between the adsorber 1 and the discharge conduit 17, by manifold 9, and way of the ports 13b and 13c. These positions correspond oppositely from valve to valve during the operation described.

Each of the adsorber vessels employed was about 12 inches long and about 11/2 inches in diameter, each having a capacity to hold about one pound of Mobilbeads with which each was packed for the operation now described. As employed, the Mobilbeads preferably may be of from

1/4 to 8 mesh size.

In this particular operation, a pressurized air stream having a moisture content of about four thousand molecular parts per million parts of air was supplied through the conduit 11. By timed energization of the solenoids 19 and 20, the valves 13 and 14 were actuated to cycle flow wet air alternately through each of the adsorbers 1 and 2. During the on cycle time, a primary effluent product was discharged from the adsorber on cycle by way of the discharge conduit opening therefrom. The wet air input through conduit 11 was adjusted by means of valves 21a and 23, to obtain a total primary effluent flow rate of about 1.0 standard cubic foot per minute. sture on the input stream to the on cycle adsorber was maintained in the vicinity of forty pounds per square inch gauge. The ambient atmosphere of the system was at about room temperature.

During the off cycle time of either adsorber, a portion of the total primary effluent product was withdrawn from the stream thereof discharged from the other or alternate adsorber and was passed through a discharge conduit such as 8 of Fig. 1. This portion was withdrawn, as through conduit 21 and 22 through the valve 21a and check valve 22a and thence by way of the conduit 7 to pass through the off cycle adsorber, in this instance adsorber 1. The primary effluent product was withdrawn from conduits 7 and 8 automatically by action of the regulating valve 21a and the differential pressure across the valve as a result of the valves 13 or 14 being closed, whereby to connect the adsorbers 1 and 2 respectively and in timed cyclical sequence with the secondary effluent

discharge conduit 17.

Withdrawal of the primary effluent product was accom-plished at the rate of about 0.5 standard cubic foot per minute. The residual effluent product stream was dis-charged by way of conduit 17. The withdrawn portion r passing through and over the adsorbent in either of the adsorbers 1 or 2, and having substantially purged the adsorbent material therein of moisture from the previous on cycle period was discharged from the system

as a secondary effluent product by way of the corresponding conduits 5 and 6, valves 13 and 14, conduits 15 and 16, the manifold 18 and the discharge conduit 17 to a zone of lower pressure, in this instance, the atmosphere.

Considering the method and apparatus described with reference to a specific procedure for drying a moist air stream as substantially typical, once a stabilized operating condition has been reached a material balance operating condition may be calculated according to the following formula:

$$R = \left(\frac{R+D}{P_1/P_0}\right)$$

In this equation R=the reflux, recycle, or purge flow rate in standard cubic feet per minute; D=the dry primary effluent product recovered from the system in standard cubic feet per minute; and P1/P0=the ratio of the adsorption cycle pressure to the desorption cycle pressure in absolute values. According to this equation, when the purge flow and recovered primary effluent product satisfy the equation, the moisture removed in the secondary effluent product in each desorption cycle will equal the moisture removed from the feed gas stream during the adsorption

If in the foregoing equation the volume of recovered primary effluent product according to the operating example given above is substituted for D in the equation and with the pressure relationships indicated, the equation becomes

$$R = \left(\frac{R+0.5}{3.7}\right) = 0.185 \text{ s.c.f.m.}$$

In other words, having reached a stabilized operating condition, it requires a purge flow of 0.185 standard cubic feet per minute to maintain that condition. As may be determined by reference to the operating condition as set forth in the example above, the purge flow there is somewhat in excess of that required according to the equation. This excess purge flow is essential initially to speed the establishment of the desired material balance. From that point on it is available through adjustment of the valve 21a to provide for greater primary effluent recovery or where circumstances may warrant to accommodate sudden increases in the content of the key component portion in the feed stream.

Fig. 2 graphically illustrates the result obtained by operation of the system in the manner described above. The air fed to the system had an initial moisture content of four thousand mol parts per million. After one day's continuous operation, cyclically reversing the flow through the adsorbers to produce an on cycle and off cycle interval of three minutes for each adsorber, the moisture content of the effluent product stream in conduits 7 and 8 had been reduced to between about fifteen and thirty mol parts per million. Over the next four days, and maintaining the original operating conditions substantially constant, the moisture content of the primary effluent product streams from the adsorber 1 and 2 was reduced to about one mol part per million, at which level it be-

came stabilized. If desired, the time required to reach a stabilized operating condition may be considerably reduced by withdrawing or diverting the entire primary effluent product of an adsorber which is on cycle to the one which is off cycle. The capacity of the adsorbers may be increased by increasing the ratio between the on cycle and off cycle pressures of the adsorbers. It may also be increased by decreasing the cycle time, although in the operation for drying air a cycle time of between about 70 one and five minutes duration is preferred, too rapid flow switching being wasteful of the feed material. Where water vapor and carbon dioxide are to be removed from the feed air stream, however, it is preferred to use activated alumina of 1/4 to 8 mesh size particles and a flow-75

10 switching cycle of about one-half minute. The capacity of the adsorbers may also be increased, of course, by increasing their volume and thereby the amounts of

adsorbent contained. In general, the capacity is increased in direct proportion to an increase in the adsorbent volume. For example, if the adsorbent is doubled, the

capacity is doubled.

In an operation such as described, employing Mobilbeads of 1/4 to 8 mesh as the adsorbent material for adsorption of water vapor from air, a preferred maximum volumetric flow through the adsorption zones is about 15 times the gross volume of adsorbent during each on cycle period. Where fine glass wool is used as the adsorbent maximum volumetric flow through the adsorption zones is preferably about 0.9 times the gross adsorbent volume. Where carbon dioxide and water vapor are key components to be removed simultaneously, and activated alumina is thus employed, a maximum volumetric flow through the adsorption zones is preferably about 2.6 times the gross volume of the adsorbent. All such flow conditions are related to and calculated at the temperature and pressure of the adsorption cycle, and under conditions of ambient temperature for the system which temperature is substantially room temperature.

As noted above, Fig. 3 and Figs. 3A to 3D inclusive schematically illustrate the manner in which a system as contemplated by the invention achieves a stabilized operat-Of these figures, Fig. 3 represents a ing condition. simple adsorption system, having a single chamber, for the purpose of indicating the fundamental concept in-Figs. 3A to 3D volved by the practice of this invention. inclusive illustrate the application of this concept to a dual adsorption chamber system, such as that represented by Fig. 1, wherein the system is initially stabilized or conditioned by repeated counterflow recycling of the total primary effluent product from each chamber to the These figures also illustrate the progressive nature of such a conditioning procedure, including the development of a moisture or vapor pressure front in the adsorb-

ent bed of each chamber.

Referring now to Fig. 3, let it be assumed that the adsorbent chamber 31 is filled with a bed 33 of adsorbent selective for a key component such as water vapor in air. If a stream of air containing water vapor with a vapor pressure of 16 millimeters of mercury at 60 pounds per square inch absolute is passed through the chamber and the adsorbent therein, by way of inlet and outlet conduits 35 and 37 respectively, at a constant number of standard cubic feet per minute, eventually the water retained by the adsorbent will reach a vapor pressure equilibrium with that of the air flowing over the adsorbent wherein it will have a vapor pressure of 16 mm. of mercury.

Now, if the inlet air stream pressure is reduced to 15 pounds per square inch absolute, with the mass flow and water vapor concentration remaining constant, the water vapor in the stream will exhibit a partial pressure of 4 millimeters of mercury. At the instant of pressure change, however, the water retained by the adsorbent still has a vapor pressure of 16 millimeters of mercury. Exposed to an environment of 4 millimeters of mercury, the retained water will adjust to this environment by giving up vapor to the air flowing over the adsorbent. Thus the adsorbent becomes drier. Initially the discharge from the chamber will contain water vapor at a partial pressure of 16 mm. of mercury. As flow continues this pressure diminishes to a point of final equilibrium at 4 mm. of mercury.

If the pressure of the inlet air stream is now returned to its initial value of 60 p.s.i.a., the water vapor contained therein again will have a partial pressure of 16 mm. Hg. As this water vapor contacts the adsorbent holding water with a partial pressure of 4 mm. Hg, water will be adsorbed from the air stream until a state of equilibrium is reached once more. The exit air stream then initially will contain water vapor at a partial pressure of 4 mm. Hg. As flow continues this partial pressure increases.

Thus, for a short time in each pressure cycle, the concentration of water vapor in the effluent air stream leaving the chamber by way of the conduit 37 will increase as the stream pressure is reduced and decrease as the stream pressure is raised. The phenomenon described is utilized according to the present invention and is further demonstrated by the conditioning of a dual chamber system described by reference to Figs. 3A to 3D inclusive.

In the apparatus represented by Figs. 3A to 3D inclusive, the numerals 41 and 42, respectively, designate two 15 adsorbent chambers. The chambers have dual purpose inlet and discharge conduit connections 45 and 47, and 46 and 50 respectively. The conduits 47 and 46 are substantially continuous through a common valve connection 51. The numerals 43 and 44 designate the selective adsorbent beds of the respective chambers 41 and 42.

Assuming the valve 51 to be wide open, if an air stream containing water vapor having a partial pressure of 16 millimeters of mercury at an initial pressure of 60 pounds per square inch absolute is introduced through conduit 45 and discharged through conduit 50, the two adsorbent beds 43 and 44 will come to equilibrium with water retained therein at a vapor pressure of 16 mm. of Hg. With the respective beds in such equilibrium condition, if the valve 51 is now set to produce a 45 pound pressure drop, the partial presure of water vapor contained in the air flowing through the bed 44 will be 4 mm. of Hg. Eventually, the bed 44 will come to equilibrium at this partial pressure, giving up water to the air which is discharged therewith by way of conduit 50.

With chamber 41 at equilibrium, and water retained

therein at a vapor pressure of 16 mm. of Hg, and chamber 42 at equilibrium with retained water therein at a vapor pressure of 4 mm. of Hg, if flow through the chambers is reversed in the manner indicated by Fig. 3B, the water vapor in the 60 p.s.i.a. stream entering chamber 42 by way of the conduit 50 will have a partial pressure of 16 mm. of Hg. The adsorbent material 44 will start to remove water from the incoming stream in an effort to achieve equilibrium, thus developing a vapor pressure front designated by the letter a. This front moves along the bed in the direction of flow therethrough. As it does so, air which contains water vapor at a partial pressure of 4 mm. of Hg moves ahead of the front and through the As the absolute pressure of this air stream is reduced 4:1 in passing through the valve, the partial pressure of contained water vapor is reduced in like fashion. As a result it enters chamber 41 with a partial pressure of 1 mm. of mercury, and develops a vapor pressure front indicated by the letter b ahead of which air with a water vapor partial pressure of 16 mm. of Hg is discharged through the conduit 45.

If the flow direction is again reversed as indicated by Fig. 3C, vapor pressure fronts, as shown, are again moved through the respective beds 43 and 44. On this cycle, the water vapor contained in the air from chamber 41, and which vapor had a partial pressure of 1 mm. of mercury in chamber 41, enters the chamber 42 with a partial pressure of ¼ mm. of mercury behind the front indicated by the letter c.

Fig. 3D illustrates the effect of another flow reversal through the chambers 41 and 42, wherein still another vapor pressure front d is developed. The water vapor behind this front now has a partial pressure of 0.0625 70 mm. of mercury due to the 4:1 reduction achieved by passage through the valve 51. By continued and frequent flow reversal, the fronts eventually merge to develop a water vapor concentration gradient along each chamber. This gradient is evidenced by the somewhat dif-

fuse but relatively well defined front which moves through the chambers in the direction of flow therethrough.

The results of the conditioning procedure just described, is further illustrated graphically by Fig. 4. The sequence of four cycles described above are represented in Fig. 4 by the graphic showing of the progress of the vapor pressure fronts through the length of the adsorber chambers. The fronts represented are lettered for identification with those shown in Figs. 3B to 3D inclusive. In Fig. 4, the fronts established when the chambers have been fully conditioned, and when a merger of preliminary fronts has been attained is designated by the letter e. The fronts developed between the fourth cycle front d and the final cycle front e are omitted in the representative showing by Fig. 4 of the progressive recession of the vapor pressure front from the effluent discharge outlet during the conditioning procedure.

When this full flow conditioning procedure is applied

when this full how conditioning procedure is applied to the system as illustrated by Fig. 1, and the primary product effluent streams through conduits 7 and 10 exhibit no measurable amount of the key component adsorbate, the pressure regulating valve 21a may be adjusted so as to obtain any desired recovery of the primary product effluent by way of the conduit 12. From this point on, the pressure cycle periods will be timed to provide for oscillatory movement of the vapor pressure front, such as represented by e in Fig. 4, in a portion of the beds intermediate the ends thereof. By so doing, the break-through of adsorbate on the adsorption cycle, or of the primary product effluent on the desorption cycle is avoided. Under such conditions, the primary product effluent recovered will have a substantially constant and extremely low partial pressure of the initially contained key component portion therein.

Thus far the invention has been described with reference to a procedure for obtaining the maximum or optimum fractionation or separation results. Under certain circumstances, as where it is desired to obtain a primary effluent in which a certain portion of the key component is retained in the primary effluent, the conditioning procedure may be altered somewhat by adjusting the recycled flow of primary effluent from one chamber to the other to a value somewhat lower than the minimum shown to be required according to the formula given above. The result obtained in this way will provide a primary effluent product containing a given percentage of the water content of the initial feed stream. If it is desired that this water content be maintained as a constant and absolute humidity value, the water content of the initial feed stream then must be regulated or controlled to provide the desired absolute humidity in the primary effluent product.

In another operation, an apparatus substantially as shown in Fig. 1, was employed to produce from atmospheric air a primary effluent product having a higher concentration of oxygen than that of the original air stream. For this operation two adsorbers, each 13 inches long by 2.875 inches in diameter were packed with 1000 grams of 5 A. molecular sieves each. Atmospheric air was supplied to the system at a pressure of seventy-five pounds per square inch. The system was at room temperature (70°-80° F.) operated substantially as described above, except that the cyclical actuation of the valves 13 and 14 was timed to produce on cycle flow for an interval of about forty seconds each. Also, in order to obtain a substantially constant primary effluent product flow, the valve timing was set to produce an overlapping on cycle flow wherein the on cycle of one adsorber was initiated about five seconds in advance of termination of the on cycle flow of the other adsorber in the pair employed. In this operation, employing a 5 A. molecular sieve as the adsorbent material, it is preferred that the maximum volumetric flow of the gaseous mixture during any on cycle period be about equal to the gross volume of the adsorbent under conditions of

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pressure and temperature as set forth above with relation to the adsorption of water vapor from air. Preliminary to a standard operation, the system was operated to determine the improvement produced by the backwashing technique contemplated by this invention. The results of such preliminary operation are indicated by the graphic showing of Fig. 5.

Measurements of oxygen concentration were made

Measurements of oxygen concentration were made with a para-magnetic oxygen analyzer (0-22%) after quantitative dilution with nitroger. In addition, the oxygen concentration was measured with a gas chromatographic analyzer calibrated for 0-100% oxygen in nitrogen. Moisture content of the oxygen-rich product varied between 2 and 6 p.m. as measured by an electrolytic moisture analyzer. Line air moisture was between 3000 and 6000 p.p.m. The apparatus dried the product in addition to concentrating the oxygen.

As indicated by Fig. 5, with a relatively large reflux flow of the primary effluent product, the inherent capacity of the adsorptive material is enhanced. As shown, 20 with cycling, but no reflux flow at all, the concentration of oxygen in the effluent product was increased from a normal concentration of about 21 mol percent in air to about 30 mol percent in the primary effluent product. As the reflux flow was started the primary effluent prod- 25 uct exhibited a tremendous increase in oxygen concentration. With a reflux flow of about 0.1 standard cubic foot per minute a maximum concentration of about 75 mol percent was exhibited. Although further increase in the reflux flow, while maintaining a constant value 30 for the primary effluent product recovery, resulted in a reduced concentration of oxygen, the least con-centration exhibited, with a reflux flow of 0.4 stand-ard cubic foot per minute, was nearly 55 mol percent, an improvement of about 25 mol percent. The results, The results, 35 as graphically illustrated, demonstrate that the effect of primary effluent product reflux is to markedly decrease the concentration of the key component in the product effluent. In this instance the key component is nitrogen.

In a commercial application of the invention, of course, primary effluent product recovery requirements might vary between large product recovery with low concentration of the nonadsorbed components and low product recovery with high concentration of nonadsorbed components. Fig. 6 demonstrates the results obtained with a constant reflux flow and with varying amounts of oxygen-rich primary effluent product recovery. The slight divergence of the curve as the recovered effluent product approached zero is assumed to be due to disturbance of the concentration gradients in the adsorbent beds due to the pressure cycling action of the system.

Referring to Fig. 7, the concentration of oxygen in the

recovered primary effluent product is plotted against the recovery flow rate of the primary effluent. The ordinates of the graph are a numerical representation of the total product flow in standard cubic feet, minus the reflux flow, multiplied by the difference between the mol per cent of oxygen in the air stream fed to the system the mol percent of oxygen determined in the effluent product. The abscissas express in standard cubic feet 60 per minute the effluent product recovered. As shown, optimum recovery with optimum oxygen concentration is attained at an effluent product recovery rate of about 0.11 standard cubic foot per minute with a total air input of about 1.00 s.c.f.m. and a secondary effluent product 65 recovery rate of about 0.795 s.c.f.m. (including reflux flow of 0.195 s.c.f.m.). This secondary effluent product contains a concentration of the key component, nitrogen, greater than in the air stream fed to the system. If desired the secondary effluent product may be accumu- 70 lated for subsequent further oxygen recovery, or for recovery of nitrogen, or it may be led directly to additional recovery systems therefor.

The apparatus and method according to the present invention may also be employed for the purpose of con- 76

14 centrating nitrogen in the primary effluent product. this operation the adsorber chambers are packed with a 4 A. molecular sieve material. Also, the valve 21a is completely closed. The backwashing action or counterflow recycle of the primary effluent product is obtained by limiting cycle time of the adsorption and desorption cycles to an extremely short period, whereby oscillation of the concentration gradient in the adsorbent material is restricted to a narrow range intermediate the ends of the bed of adsorbent material and of the chamber. operating in this fashion the chamber portion adjacent the outlet for primary effluent product serves as an accumulator zone for such product, whereby it is available for counterflow backwashing when pressure on the chamber is reduced. This includes the product portions which may be held in the pores of the adsorbent as well as in the interstitial spaces of the bed beyond the oscillatory gradient front.

As an example of the procedure for concentrating nitrogen in a primary effluent product, two chambers 13" long x 2.875" in diameter were each filled with 1,000 grams of 4 A. molecular sieve material. Atmospheric air was supplied to the inlet 11 of the apparatus as shown in Fig. 1 at a pressure of 85 pounds per square inch absolute. The cycle timers 19 and 20 were set so as to actuate valves 13 and 14 at ten second intervals whereby flow of the air fed to the system was directed alternately into the adsorbent chambers 1 and 2, and so that while one chamber was on cycle the other chamber was off cycle and open to the atmosphere at a pressure of about 15 pounds per square inch absolute, by suitable action of the valves as previously described.

By operation in this fashion, nitrogen-rich primary effluent product flow was obtained wherein the primary effluent product contained as little as ¾ % oxygen. effectiveness of the operation is illustrated graphically by Fig. 8. By suitable adjustment of the valve 23 in line 12 in the apparatus as shown in Fig. 1, primary effluent product flow was varied between 0 and 1.2 standard cubic feet per minute. As shown, concentration of nitrogen in the primary effluent product ranged from 99.25% to about 65% of the primary effluent product, as determined by the percentage of oxygen present in the primary product effluent. In Fig. 8 the dotted lines extending from points on the abscissa and ordinate of the graph scale to intersect in the graph curve indicate an optimum condition. As shown by the graph, under optimum conditions, product flow was 0.8 standard cubic foot per minute and contained 10.5% oxygen. Under these conditions, the secondary effluent product flow discharged by way of the line 17 of figure was 0.2 standard cubic foot for each desorption cycle. At six cycles per minute, therefore, the total secondary effluent discharge was 1.2 standard cubic feet per minute. Thus, the total discharge of primary and secondary effluent products was 1.2 plus 0.8 or 2.0 standard cubic feet per minute, substantially equaling the feed rate of atmospheric air. The incoming air, of course, had a nitrogen content of approximately 78% or 1.56 standard cubic feet per minute of the 2.0 cubic feet per minute fed into the system. As shown by Fig. 7 at optimum conditions the primary effluent product contained 10.5% oxygen. Additionally, it may contain about 1% argon, or a total of 11.5% diluent components. Thus, the primary effluent product contained approximately 88.5% nitrogen or 0.71 standard cubic foot per minute of the total 0.8 cubic foot of primary effluent product. Relating this recovery to the 1.56 standard cubic feet per minute of nitrogen in the feed air stream, the nitrogen recovery of the method is therefore approximately 45%, indicating an extremely efficient separating technique without the need for extreme pres-sure and temperature operating conditions. Although the foregoing calculations are based only on the content of nitrogen, oxygen and argon in the incoming feed stream, it is to be noted that both water vapor and carbon dioxide

in the original feed will be separated by the adsorbent material and discharged with the secondary effluent

Fig. 9 diagrammatically illustrates a system which may be operated according to the method of the present invention whereby to concentrate both oxygen and nitrogen from atmospheric air, and wherein the secondary effluent product discharged from separate nitrogen and oxygen concentrating components of the system is em-ployed to enrich the air feed stream supplied thereto. 10 The apparatus combination illustrated by Fig. 9 employs a series of adsorber systems similar to the one illustrated by Fig. 1. These systems are combined and employed for the purpose of fractionating atmospheric air to produce two product streams of which one is rich in nitro- 15 gen and the other is rich in oxygen. In the method con-templated by this combination the secondary effluent product of one adsorber concentration system is crosscycled so as to provide at least a portion of the feed for the other adsorber concentration system.

In the combination illustrated, four adsorber systems are employed. In each system the component parts are designated by numerals directly comparable with those to designate similar parts in the system illustrated by Fig. 1 except that the numerical designation will be in either a 100, 200, 300 or 400 series. Thus the system for concentrating oxygen is in the 300 series while the system for concentrating nitrogen is in the 400 series. The systems for removing moisture and carbon dioxide from the feed to each of the nitrogen and oxygen concentration systems are numbered in the 100 and 200 series respectively. Thus the feed to the nitrogen concentration system passes through a drier system numbered in the 100 series, while the feed to the oxygen concentration system passes through a drier system numbered in 35

the 200 series.

Each of the drier systems includes an inlet conduit 111 and 211 respectively, connected to the discharge of a compressor or pump 100b and 200b respectively. The inlets of the respective pumps are connected to conduits which include non-mixing air surge tanks 100a and 200a respectively. These tanks are each packed with an inert loose granular or fibrous material such as glass wool, glass beads, aluminum pellets, etc., which offer a sub-stantial resistance to mixing. The tanks open to the atmosphere at one end and as indicated are connected at the other end to the inlet of a compressor pump 100b or 200b. The primary effluent product discharge from each of the adsorbers systems in the 100 or 200 series is delivered by means of the conduits 112 and 212 respectively to accumulator chambers 100c and 200c respectively. Thence, these primary product effluents are delivered to the respective nitrogen and oxygen concentrator systems by way of feed conduits 411 and 311 respectively. Provision is made in the apparatus combination illustrated for cross-cycling the secondary effluent product of each of the 300 and 400 series systems by cross-connection of the secondary effluent product discharge conduits 317 and 417 to the inlets of the compressors 100b and 200b respectively, intermediate these compressors and their associated surge tanks 100a and 200a.

In the apparatus combination as illustrated by Fig. 9, the two compressor pumps, 100b and 200b, inspirate air from the atmosphere through the respective surge tanks 100a and 200a. The pump 100b feeds the drier system in which the component parts are designated by numerals The feed stream from pump 100b in the 100 series. enters this system through the conduit 111 at a pressure, for example, of about 65 pounds per square inch absolute, and is cycled between the adsorber chambers 101 and 102 substantially in the manner described with reference to Fig. 1. In this system, the adsorbent material preferably will be one selective for water vapor, carbon dioxide and trace contaminants such as hydrocarbon vapors. A suitable adsorbent for this purpose is activated alumina. 16

This system also employs a recycle or reflux purge stream derived from the primary effluent product of the ad-sorber on cycle to backwash the adsorbent material in the adsorber which is off cycle. The secondary effluent product in this system is a mixture of air, water vapor, carbon dioxide, and other trace contaminants, and is discharged directly to the atmosphere through the valves 113 and 114 depending upon which adsorber is on the desorption cycle. At the same time the compressor 200b inspirates a stream of atmospheric air through the conduit which includes the surge tank 200a, discharging air, at approximately 65 pounds per square inch absolute, into the inlet conduit 211 of the drier system in which the component parts are numbered in a 200 series. this system, also the adsorber chambers 201 and 202 are packed with activated alumina for the purpose of fractionating or separating water, carbon dioxide and other trace contaminants in the same fshion as the 100 series adsorber system, and discharging the separated key component portion of the feed stream as a secondary effluent product by way of the valves and connecting conduits including valves 213 and 214.

The respective drier systems discharge a primary effluent product, which is air from which water, carbon dioxide and other contaminants have been removed by way of their respective discharge conduits 112 and 212. The conduit 112 communicates with an accumulated chamber 100c, while the conduit 212 communicates with

a separate accumulator chamber 200c.

From the accumulators 100c and 200c, the primary effluent product of the related 100 and 200 series drier systems is passed respectively to the nitrogen and oxygen concentrator systems. As previously mentioned, 4 A. molecular sieve material has been found to be an excellent adsorbent for selectively removing oxygen from air, whereby to concentrate nitrogen in the primary effluent product of the system. In the apparatus represented and illustrated by Fig. 9, the adsorber chambers
401 and 402 are preferably packed with this material.
The primary effluent product delivered to the accumulator 200c by way of the discharge line 212 is passed therefrom through lines 311 to the feed inlet of the adsorber system for concentrating oxygen. In this system the ad-sorber chambers 301 and 302 may be packed with either 5 A. or13 A. molecular sieve material, these materials as indicated above having a selective affinity for nitrogen whereby the primary effluent product discharged by way of the line 312 will be an oxygen-rich product.

In each of the nitrogen and oxygen concentrating systems the secondary effluent product, which in the first in-stance will be relatively rich in oxygen, and in the second instance relatively rich in nitrogen is cross-cycled to the inlet of the compressor pump providing the initial feed for the oxygen and nitrogen adsorber systems respectively. Thus the secondary product effluent from the isorbers 401 and 402 is discharged by way of conduits 415 and 416, 418 and 417, of which the latter is connected to the inlet to the compressor 200b downstream from the surge chamber 200a. The secondary effluent product from the adsorbers 301 and 302 is discharged by way of the conduits 315, 316, 318 and 317, of which the latter is connected to the inle. of the compressor pump 100b downstream from the surge tank 100a. The surge tanks 100a and 200a are adapted to avoid loss of the secondary effluent products from the respective nitrogen and oxygen concentrators. It is contemplated that each tank will have a volume adequate to accommodate the volume of gas in standard cubic feet which is discharged from one of the adsorber chambers in the nitrogen and oxygen concentrating systems when the pressure in the chamber is reduced from the adsorbing pressure of any given value to a pressure approximating that of the atmosphere.

As previously indicated, each of the adsorber systems in the combination apparatus of Fig. 9 is comparable to the system as illustrated by Fig. 1. Likewise, the drier systems in this combination are operated according to the method recited in connection with Fig. 1 as are the oxygen and nitrogen concentrating systems. Each system may be provided with its own cycle timer (not shown) and the cycle period adjusted to provide the most efficient operation conditions.

Although the description as set forth above exemplifies the method with reference to its employment for certain specific purposes, the invention is not to be considered as especially limited to such use. Other gaseous mixtures may be purified and concentrated by the fractionation procedure set forth, wherein a component portion of a gaseous feed material is adsorbed and desorbed cyclically by a bed of an adsorbent material selective therefor under cycling differential pressure conditions; wherein a concentration gradient of the adsorbed material having a low concentration front is oscillated in an area of the adsorbent bed intermediate the ends thereof; and wherein during the desorption cycles, at least a portion of the primary effluent product of the adsorp-tion step is passed through the adsorbent bed in counterflow relation to the flow direction of the feed material

during the adsorption cycles.

As pointed out above, the present invention is concerned with a method of fractionating a gaseous material. In essence, the operation comprises flowing a stream of gaseous material through a bed of adsorbent at a pre-selected initial pressure and flow direction. The adsorbent is selective for at least one component fraction of said material. The stream is flowed through the bed for a first cycle period less than that required for the bed to come to equilibrium with the component fraction. A primary effluent product comprising an unadsorbed portion of the feed stream is discharged from the bed. At the end of the first cycle period, the flow of the feed stream is interrupted and the initial pressure on the bed reduced. The adsorbed components are desorbed from the bed at the reduced pressure. These desorbed com-ponents are discharged from the bed in a flow direction opposite to the flow direction of the feed stream of the gaseous material for a second cycle period. During the second period at least a portion of the primary effluent product is passed through the bed in a flow direction of the desorbed component fraction. This latter mixture comprising a portion of the primary effluent product and the desorbed component is discharged from the bed as a secondary effluent product. The cycle periods are adjusted for a time duration adapted to develop a con-centration gradient of the component fraction in said bed wherein the gradient has a front of lowest concentration in a zone intermediate the ends of the bed. An oscillatory movement is imparted to the front substantially within the limits of the zone in a direction and for a distance which corresponds respectively to the direction of the flow through the bed during each cycle period and to the duration thereof.

What is claimed is: 1. A process for the removal of a key component from a gaseous mixture stream utilizing two adsorbent beds each of which is characterized by having a one end and an other end, said process comprising the steps of flowing a feed stream of a gaseous mixture including a key component from one end to the other end through a first bed of an adsorbent initially relatively free of said by component at a preselected initial relatively high pressure and in a positive flow direction in an initial cycle, said adsorbent being preferentially selective for said key component; discharging said gaseous mixture stream from said first bed as a primary effluent; segregating a portion of said primary effluent as a product stream and withdrawing the same; passing the remainder of said primary effluent in reverse flow from the other end to the one end through a second bed of adsorbent at a relatively low pressure, which adsorbent is rela- 75 of about 5 Angstroms.

18 tively saturated with said key component as compared to said first bed at the start of said inital cycle, whereby as said initial cycle continues, said first bed becomes relatively saturated with said key component progressively from said one end toward said other end, and whereby said second bed becomes relatively freed from said key component from said other end toward said one end; continuing said initial cycle for a time period less than that required to secure saturation of said first bed at said other end and that required to secure freedom from said key component of said second bed at said one end; thereafter introducing said feed stream into said one end of said second bed in positive flow direction at said initial relatively high pressure; discharging said gaseous mixture stream from said other end of said second bed as a primary effluent; segregating a portion of said last named primary effluent as a product stream and withdrawing the same; passing the remainder of said last named primary effluent in reverse flow from said other end to said one end through said first bed of adsorbent at said relatively low pressure, and thereafter cyclically

continuing the operation.

2. A method of fractionating a gaseous mixture of at least two components comprising, at a preselected initial relatively high pressure and initial positive flow direction, flowing a first feed stream of said gaseous material through a first bed of adsorbent selective for a first component of said gaseous mixture, for a first cycle period less than required for said first bed to come to equilibrium with said first component; flowing a second feed stream of said gaseous mixture through a second bed of an adsorbent selective for a second component of said gaseous mixture, for a first cycle period less than required for said second bed to come to equilibrium with said second component; discharging the unadsorbed portion of each said first and second streams from said first and second beds as first and second primary effluent streams respectively; interrupting flow of each said first and second feed streams at the end of said first cycle period and reducing said initial pressure on each said first and second beds; desorbing each said first and second components from said respective first and second beds at said reduced pressure, and discharging said desorbed first and second components from said respective beds in a flow direction opposite to that of said first and second feed streams of said gaseous material, during said second period flowing at least a portion of said first and second primary effluent streams respectively through said first and second beds in the flow direction of said component desorbed therefrom and discharging said first and second primary effluent portions from said respective beds together with said first and second components desorbed from said beds as secondary effluent streams; adjusting said cycle periods for a duration adapted to develop in each said first and second beds a concentration gradient of said respective first and second components in said respective beds; imparting oscillatory movement to said fronts substantially within the limits of said zones in a direction and for a distance which correspond respectively to the direction of flow through said beds during each cycle period and to the duration thereof; and preferentially flowing at least a portion of said secondary effluent streams discharged from said first and second beds during said second cycle period through said second and first beds respectively during said first cycle period; and conducting the frac-tionation in a manner that substantially the sole transfer of heat to and from the gas occurs in said beds.

3. A method according to claim 1, wherein said gase ous mixture is air and said component includes water

vapor.

4. A method according to claim 1 wherein said gaseous mixture is air, and said component includes nitrogen.

5. A method according to claim 4, wherein said adsorbent is a molecular sieve material having a pore size 19

6. A method according to claim 4, wherein said adsorbent is a molecular sieve material having a pore size of about 13 Angstroms

7. A method according to claim 1, wherein said gaseous mixture is air, and said component includes oxygen.

8. A method according to claim 7, wherein said adsorbent is a molecular sieve material having a pore size

of about 4 Angstroms.

9. A method of fractionating a gaseous mixture of at least two components consisting essentially of the steps 10 of flowing a feed stream of said gaseous mixture at a preselected initial relatively high pressure and in an initial positive flow direction through a fixed bed of an adsorbent, selective for at least one component of said mixture for a first cycle time period less than required for said 15 bed to come to equilibrium with said component, discharging the unadsorbed portion of said feed stream as a primary effluent stream; interrupting flow of said feed stream at the end of said first cycle period and reducing said initial pressure on said bed at the inlet end, desorbing said component from said bed at a reduced pressure, and discharging said desorbed component from said bed in a flow direction opposite to that of said feed stream of gaseous material, for a second cycle time period, during said second time period flowing at least a portion of 25 said primary effluent stream through said bed in the flow direction of said desorbed component and discharging said portion of primary effluent portion from said bed together with said desorbed component as a secondary effluent stream; said time periods being each of such short 30 duration that the heats of adsorption and desorption are substantially balanced within said bed and that substantially the sole transfer of heat to and from the gas occurs in said bed, thereby eliminating the need for the transfer of heat externally with respect to said bed; adjusting said 35 cycle periods for a duration adapted to develop an oscillating concentration gradient of said component in said bed which remains in the bed during both the adsorption and desorption cycle, and imparting oscillatory movement to said front substantially within the limits of said bed.

10. Process as defined by claim 9 wherein said feed stream comprises air, wherein said one component comprises water vapor, wherein said adsorbent is selected from the class consisting of alumina, silica gel, and Mobilbeads of ½ to 8 mesh and wherein said first cycle period is less than that required for a total volume of air equivalent to fifteen times the gross volume of said adsorbent to flow through said bed, said air volume being

measured at the temperature and pressure existing in said bed on the adsorption cycle.

11. Process as defined by claim 9 wherein said gaseous material comprises air, wherein said adsorbent comprises a molecular sieve and wherein said component comprises nitrogen.

12. Process as defined by claim 1 wherein the time of 65 each cycle is for a time period so that the partial pressure of the key component in the gas phase at the discharge end of said second bed does not deviate substantially from the partial pressure of the key component

in the gas phase at the inlet of said first bed. 13. A process for the removal of water vapor from a gaseous mixture stream comprising flowing a feed stream of gaseous mixture comprising water vapor from one end to the other end through a first bed of a relatively dry adsorbent at a preselected initial relatively high pressure and in a positive flow direction in an initial cycle, said adsorbent being preferentially selective for said water vapor, discharging the dry portion of said gaseous mixture stream from said first bed as a primary effluent, segregating a portion of said primary effluent as a dry product stream and withdrawing the same, passing the re-mainder of said primary effluent in reverse flow from one end to the other end through a second bed of adsorbent at a relatively low pressure which adsorbent is relatively saturated with water vapor as compared to said first bed 78

20 at the start of said initial cycle, whereby as said initial cycle continues, said first bed becomes relatively saturated with water vapor progressively from said one end toward said other end, and whereby said second bed becomes progressively relatively dry from the one end toward said other end, continuing said initial cycle for a time period less than that required to secure complete saturation of said first bed at said other end and that required to secure complete dryness of said second bed at said other end, thereafter introducing said feed stream into said second bed at said other end in positive flow direction at said initial relatively high pressure, discharging the dry portion of said gaseous mixture stream from said one end of said second bed as a primary effluent, segregating a portion of said primary effluent as a dry product stream and withdrawing the same, passing the remainder of said primary effluent in reverse flow from said other end to said one end through said first bed of adsorbent at said relatively low pressure, and thereafter cyclically continuing the operation.

14. Process as defined by claim 13 wherein the time of each cycle is for a time period so that the partial pressure of the water vapor in the gas at the discharge end of said second bed does not deviate subsantially from the partial pressure of the water vapor in the gas

at the inlet of said first bed.

15. Process as defined by claim 13 wherein a region of lowest concentration of moisture continually exists on said adsorbent material intermediate the point of introduction of said mixture stream into said first bed and the point of withdrawal of said secondary effluent product from said second bed.

16. Operation as defined by claim 13 wherein said cycle is maintained for a time period sufficiently short so that the temperature of said beds is substantially

ambient.

17. Operation as defined by claim 13 wherein said beds are self-contained with respect to the transfer of heat.

18. A method for fractionating a gaseous mixture, comprising cyclically and alternately flowing a feed stream of said mixture at a selected initial relatively high pressure through each of two confined adsorption zones into contact with an adsorbent material contained in each, said adsorbent being selective for at least one key component portion of said mixture; progressively adsorbing at least said key component portion from said mixture stream in one of said zones at said selected relatively high pressure, whereby an increasing concentration gradient of said key component on said adsorbent will advance in the direction of flow; discharging said feed stream from said one zone, under substantially the initial pressure thereof, as a primary effluent product; withdrawing at least a portion of said primary effluent product discharged from said one zone; flowing said withdrawn portion through the other of said zones at a secondary relatively low pressure in a counterflow direction relative to the flow direction of said initial stream through each of said zones; progressively desorbing said key component portion previously adsorbed therein, whereby a decreasing concentration gradient of said key component or, said adsorbent will advance in the direction of counterflow and discharging a secondary effluent product from said other zone, said secondary effluent product comprising said portion of said primary effluent product and said key component portion, carrying out said cycles for time periods whereby said key component is never completely removed from either zone, and conducting said operation in a first phase under conditions that the volume of said portion of said primary effluent product at said relatively high initial absolute pressure bears a greater ratio to the total volume of said primary effluent than said relatively low absolute pressure bears to said relatively high pressure until a predetermined degree of saturation is attained in said zones, and thereafter in a second phase continuing said operation under conditions wherein the volume of

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said portion of said primary effluent product at said high pressure bears substantially the same ratio to the volume of said primary effluent as said low pressure bears to

said high pressure.

19. Process as defined by claim 18 wherein R represents said portion of said primary effluent product in s.c.f.m., wherein (R+D) represents said primary effluent product in s.c.f.m., wherein P1 represents said initial absolute pressure and Po represents said secondary absolute pressure; carrying out the operation in said initial phase 10 in a manner that R is greater than

R+D $P_1/P_0$ 

and wherein in said second phase R substantially equals 15

R+D $P_1/P_0$ 

20. Process as defined by claim 18 wherein in said first 20 phase said portion of said primary effluent product flowed to said other zone comprises essentially said primary

effluent.

21. A method for fractionating a gaseous mixture, comprising cyclically and alternately flowing a feed stream 25 of said mixture at a selected initial relatively high pressure through each of two contined adsorption zones into contact with an adsorbent material contained in each, said adsorbent being selective for at least one key component portion of said mixture; progressively adsorbing at least said key component portion from said mixture stream in one of said zones at said selected relatively high preswhereby an increasing concentration gradient of said key component on said adsorbent will advance in the direction of flow; discharging the remainder of said mixture stream from said first zone, under substantially the initial pressure thereof, as a primary effluent product; withdrawing at least a portion of said primary effluent product discharged from said one zone; flowing said withdrawn portion through the other of two said zones at a secondary relatively low pressure in a counterflow direction relative to the flow direction of said initial stream through each of said zones; progressively desorbing said key component portion previously adsorbed therein, whereby a decreasing concentration of said key component on said adsorbent will advance in the direction of flow and discharging a secondary effluent product from said other zone, said secondary effluent comprising said portion of said primary effluent product and said key component portion, carrying out said cycles for time periods whereby said key component is never completely removed from either zone and conducting said operation under conditions that the total volume of said primary effluent divided by the volume of primary effluent passed to said other zone is less than the absolute high pressure divided by the absolute low pressure.

22. Process as defined by claim 21 wherein R represents said portion of said primary effluent product in s.c.f.m., wherein (R+D) represents said primary effluent product in s.c.f.m., wherein P1 represents said initial pressure and Po represents said secondary pressure; carrying out the operation in a manner that R is somewhat greater

than

 $P_1/P_0$ 

23. Process as defined by claim 13 wherein said gaseous

mixture comprises air.

24. Process as defined by claim 13 wherein the volume of primary effluent passed to said second bed at said high pressure is about the same ratio to the total volume of primary effluent as the ratio of the absolute pressure of the low pressure unit is to the absolute pressure of the high pressure unit.

25. A method for fractionating a gaseous mixture stream comprising oxygen and nitrogen, comprising flow- 75 22

ing a feed stream of said mixture at a selected initial relatively high pressure through a confined adsorption zone into contact with an adsorbent material, said adsorbent being selective for oxygen of said mixture contained in said zone under conditions that the heats of adsorption and desorption are substantially balanced within said zone, and conducting the fractionation in a manner that substantially the sole transfer of heat in said zone occurs between said material and said stream flowing therethrough, progressively adsorbing oxygen from said mixture stream in said zone, whereby an increasing concentration gradient of oxygen on said adsorbent will advance in the direction of flow; discharging the remainder of said mixture stream from said zone, under substantially the initial pressure thereof, as a nitrogen-rich effluent product stream, thereafter at the inlet end reducing the pressure to a secondary relatively low pressure and progressively desorbing said oxygen adsorbed therein, whereby a decreasing concentration of said oxygen on said adsorbent will advance in the direction of counterflow, and dis-charging a secondary oxygen-rich effluent product stream from said zone at the end at which said feed stream was introduced and carrying out said cycles for time periods whereby said oxygen component is never completely removed from said zone and whereby an oxygen concentration gradient will remain in said zone during both the adsorption and desorption cycle.

26. An apparatus for adsorptive fractionation of a gaseous mixture, said apparatus comprising (1) two separately defined chamber vessels, (2) a body of adsorbent material in each of said vessels, said bodies being preferentially adsorptive of at least one and the same component of said mixture, (3) primary inlet conduit means connected to each of said vessels wherethrough said gaseous mixture may be supplied to said vessels, (4) valve means in said primary inlet conduit means whereby the supply of said gaseous mixture to said vessels may be alternated from vessel to vessel, (5) primary outlet conduit means connected to each of said vessels where-through gaseous material may be removed from said vessels as a primary effluent product, said primary outlet conduit means and said primary inlet conduit means being so connected to said vessels to establish therebetween in each vessel a primary path of flow of gaseous material through each of said bodies of adsorbent material, (6) reflux conduit means connected to each of said vessels wherethrough at least a portion of said primary effluent product removed from either of said vessels may be directed into the other vessel, said reflux conduit means including pressure regulating control valve means whereby a substantially constant preselected pressure may be maintained downstream of said control valve means in the direction of said other vessel for a range of pressures of reselected said primary effluent product exceeding sa... pressure, (7) secondary outlet conduit mea. connected to each of said vessels wherethrough gaseous material may be removed from said vessels as a secondary effluent product, said secondary outlet conduit means and said reflux conduit means being so connected to said vessels to establish therebetwen in each vessel a secondary path of flow of gaseous material through each of said bodies of adsorbent material which is substantially coincident with and opposite in direction to said primary path of flow therethrough, and (8) valve means in said second-ary outlet conduit means whereby the removal of said secondary effluent product from said vessels may be alternated from vessel to vessel.

27. An apparatus according to claim 26 in which said valve means in said primary inlet conduit means and said valve means in said secondary outlet conduit means together comprise two three-port valves, one of which may alternately permit supply of said gaseous mixture into and removal of said secondary effluent product from one of said vessels, and the other of which may alternately permit supply of said gaseous mixture into and removal of said secondary effluent product from the other of said vessels.

28. An apparatus according to claim 26 which includes actuating means for said valve means in said primary inlet conduit means and said valve means in said secondary outlet conduit means whereby both said valve means are alternately and cyclically thrown to permit start of supply of said gaseous mixture to a first one of said vessels at least no later than start of removal of said secondary effluent product from a second one of said vessels and start of supply of said gaseous mixture to said second one of said vessels at least no later than start of removal of said secondary effluent product from said first one of said

29. An apparatus for adsorptive fractionation of a 15 gaseous mixture whereby at least two gaseous primary effluent products may be generated, one of said primary effluent products being relatively rich in one of said components of said mixture and the other of said primary effluent products being relatively rich in another of said 20 components thereof, said apparatus comprising (1) separately defined first and second chamber vessels, (2) a body of adsorbent material in each of said first and second vessels, said bodies being preferentially adsorptive of only one and the same of the components of said 25 gaseous mixture in which one of said primary effluent products is relatively rich, (3) first primary inlet conduit means connected to each of said first and second vessels wherethrough gaseous material may be supplied to said vessels, (4) valve means in said first primary inlet conduit means whereby the supply of gaseous material to said first and second vessels may be alternated from vessel to vessel, (5) first primary outlet conduit means connected to each of said first and second vessels wherethrough gaseous material may be removed from said vessels as a first primary effluent product, said first primary outlet conduit means and said first primary inlet conduit means being so connected to said first and second vessels to establish therebetween in each vessel in a primary path of flow of gaseous material through each of said bodies 40 of adsorbent material in said vessels, (6) first secondary outlet conduit means connected to each of said first and second vessels wherethrough gaseous material may be re-moved from said vessels, said first secondary outlet conduit means being so connected to said first and second vessels with respect to the connection of said first primary outlet conduit means thereon to establish therebetween in each vessel a secondary path of flow of gaseous material through each of said bodies of absorbent material in said vessels which is substantially coincident with and op-posite in direction to said primary path of flow there. 50 through, (7) valve means in said first secondary outlet conduit means whereby the removal of gaseous material from said first and second vessels through said first secondary outlet conduit means may be alternated from vessel to vessel, (8) separately defined third and fourth chamber vessels, (9) a body of adsorbent material in each of said third and fourth vessels, said bodies each being preferentially adsorptive of the other only of the components of said gaseous mixture in which one of said primary effluent products is relatively rich, (10) second primary inlet conduit means connected to each of said third and fourth vessels wherethrough gascous material may be supplied to said vessels, (11) valve means in said second primary inlet conduit means whereby the supply of gaseous material to said third and fourth vessels may be alternated from vessel to vessel, (12) second primary outlet conduit means connected to each of said third and fourth vessels wherethrough gaseous material may be removed from said vessels as a second primary effluent product, said second primary outlet conduit means and said second primary inlet conduit means being so connected to said third and fourth vessels to establish therebetween in each vessel a primary path of flow of gaseous material through each of said bodies of adsorbent material in said vessels, (13) second secondary outlet conduit means connected to each 75 first and second vessels wherethrough at least a portion of

24 of said third and fourth vessels wherethrough gaseou material may be removed from said vessels, said second secondary outlet conduit means being so connected to said third and fourth vessels with respect to the connections of said second primary outlet conduit means thereon to establish therebetween in each vessel a secondary path of flow of gaseous material through each of said bodies of adsorbent material in said vessels which is substantially coincident with and opposite in direction to said primary path of flow therethrough, (14) valve means in said second secondary outlet conduit means whereby the removal of gaseous material from said hird and fourth vessels through said second secondary outlet conduit means may be alternated from vessel to vessel. (15) first compressor means designed to handle gaseous material and characterized by suction and discharge regions, said first compressor means being so connected at its discharge region to said first primary inlet conduit means that compressed gaseous material leaving said first compressor means may flow toward either of said first and second vessels according to the setting of said valve means in said first primary inlet conduit means. (16) second compressor means designed to handle gaseous material and characterized by suction and discharge regions, said second compressor means being so connected at its discharge region to said second primary inlet conduit means that compressed gaseous material leaving said second compressor means may flow toward either of said third and fourth vessels according to the setting of said valve means in said second primary inlet conduit means, (17) first supply conduit means wherethrough a stream of said gaseous mixture may be furnished from a source of said mixture, said first supply conduit means being connected to the suction region of said first compressor means, (18) second supply conduit means wherethrough a stream of said gaseous mixture may be furnished from a source of said mixture, said second supply conduit means being connected to the suction region of said second compressor means, (19) first transfer conduit means connected between said first secondary outlet conduit means and said second supply conduit means wherethrough gaseous material may flow to said second supply conduit means from either of said first and second vessels according to the setting of said valve means in said first secondary outlet conduit means, and (20) second transfer conduit means connected between said sec ond secondary outlet conduit means and said first supply conduit means wherethrough gaseous material may flow to said first supply conduit means from either of said third and fourth vessels according to the setting of said valve means in said second secondary outlet conduit means.

30. An apparatus according to claim 29 which includes a surge chamber in each of said first and second supply conduit means, said chambers being further respectively from the suction regions of said first and second compressor means than are the connections of said second and first transfer conduit means on said first and second supply conduit means.

31. An apparatus according to claim 29 which includes actuating means for said valve means in said first primary inlet conduit means, said valve means in said first sec ondary outlet conduit means, said valve means in said second primary inlet conduit means, and said valve means in said second secondary outlet conduit means whereby said several valve means are alternately and cyclically thrown to permit start of supply of gaseous material to said first and third vessels at least no later respectively than start of removal of gaseous material from said second and fourth vessels and start of supply of gaseous material to said second and fourth vessels at least no later respectively than start of removal of gaseous material from said first and third vessels.

32. An apparatus according to claim 29 which includes reflux conduit means connected to each of at least said 25

said first primary effluent product removed from either of said vessels may be directed into the other vessel, said reflux conduit means including pressure reducing means, and said reflux conduit means being so connected to said first and second vessels with respect to the connections of said first secondary outlet conduit means thereon to establish therebetween in each vessel a path of flow of gaseous material through each of said bodies of adsorbent material from said reflux conduit means to said first secondary outlet conduit means which is substantially coincident with and opposite in direction to said primary

path of flow therethrough. 33. An apparatus according to claim 29 which includes (1) a first preliminary adsorptive fractionating means preferentially adsorptive of at least one component of 15 said gaseous mixture other than the components in which said first and second primary effluent products are relatively rich and substantially non-adsorptive of either of said latter components, said first preliminary adsorptive fractionating means having an inlet region for receiving ous material to be preliminarily fractionated therein and an outlet region for discharging non-adsorbed gaseous material, and said first preliminary adsorptive fractionating means being installed intermediate said discharge region of said first compressor means and said first primary inlet conduit means with its inlet region connected to said discharge region of said first compressor means, (2) a second preliminary adsorptive fractionating means preferentially adsorptive of at least one component of said gaseous mixture other than the components in which 30 said first and second primary effluent products are relatively rich and substantially non-adsorptive of either of said latter components, said second preliminary adsorp-tive fractionating means having an inlet region for receiving gaseous material to be preliminarily fractionated therein and an outlet region for discharging non-adsorbed gaseous material, and said second preliminary adsorptive fractionating means being installed intermediate said discharge region of said second compressor means and said second primary inlet conduit means with its inlet region 40 connected to said discharge region of said second compressor means, (3) a first accumulator chamber installed intermediate said outlet region of said first preliminary adsorptive fractionating means and said first primary inlet conduit means, and (4) a second accumulator chamber installed intermediate said outlet region of said second preliminary adsorptive fractionating means and said second primary inlet conduit means

34. Process as defined by claim 13 wherein the time of each cycle is for a time period so that substantial equilibrium exists between the moisture in the feed stream and on the adsorbent at said one end of said first bed,

and that substantial equilibrium exists between the moisture in the gas and on the adsorbert at said other end

of said second bed. 35. A method for fractionating a gaseous mixture comprising flowing a feed stream of said mixture at a selected initial relatively high pressure into one end and through a confined adsorption zone into contact with an adsorbent material selective for at least one component of said mixture, progressively adsorbing said one component from said mixture stream in said zone, whereby an increasing concentration gradient of said one compo-nent on said adsorbent will advance in the direction of flow, discharging gaseous effluent stream from the other end of said zone, under substantially the initial pressure thereof, thereafter stopping the flow of said feed stream, reducing the pressure at said one end to a secondary relatively low pressure and withdrawing a gas stream from said one end, thereby progressively desorbing said one component from said adsorbent and backflowing said desorbed one component toward said one end, whereby a decreasing concentration of said one component on said adsorbent will advance in the direction of backflow, and discharging said one component from said zone at said one end at which said feed stream was introduced, conducting said operation for time periods so that the heats of adsorption and desorption are substantially balanced within said zone, and conducting the fractionation in a manner that substantially the sole transfer of heat to and from the gas in said zone occurs in said bed thereby eliminating the transfer of heat externally with respect to said zone, and conducting the fractionation under conditions whereby an oscillating concentration gradient of said one component will remain in said zone during both the adsorption and desorption cycle, and said gradient will have a front of lowest concentration intermediate the

ends of said zone.

36. Process as defined by claim 25 wherein said adsorbent comprises 4 A. molecular sieves.

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### PLAINTIFF'S EXHIBIT 5B

Kahle German Patent No. 871,886 and Translation



Erreilt auf Grund des Ersten Überleitungsgesetzes vom 8. Juli 1949

#### BUNDESREPUBLIK DEUTSCHLAND



AUSGEGEBEN AM 26. MXRZ 1953

**DEUTSCHES PATENTAMT** 

## PATENTSCHRIFT

M: 871 886 KLASSE 12e GRUPPE 302 G: 105 IV b / 12e

Dipl.-Chem. Dr. Bug. Heinrich Kahle, Pullach bei München ist als Erfinder genannt worden

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#### Adsorptionsverfahren

Patentiert im Gebiet der Bundesrepublik Deutschland vom 2. Juli 1942 an Der Zeitraum vom 8. Mai 1945 bis einschließlich 7. Mai 1950 wird auf die Patentdauer nicht angerechnet (Ges. v. 15. 7. 51)

Patentanmeldung bekanntgemacht am 27. September 1951
Patenterteilung bekanntgemacht am 19. Februar 1953

Es ist bekannt, zur Entfernung oder Gewinnung von Mischungsbestandteilen aus Gasgemischen Adsorptionsverfichren anzuwenden und mit Adsorptionsmitteln gefüllte Behälter, die sogenannten Adsorbtionsmitteln gefüllte Behälter, die sogenannten Adder Ausorption und Desorption periodisch umgeschaltet werden. Bei der Desorption durch Spüllung mittels eines Gases oder durch Evakuierung wird das Gas in der Regel in entgegengesetzter Richtung zur Gasströnnung während des Adsorptionsvorganges geführt. Man war bisher bestrebt, vor Beginn jedes einzelnen Adsorptionsvorganges das Adsorptionsmittel möglichst weitgehend zu desorbieren.

12.

1:

Erhadungsgemäß wird von dieser Regel erheblich besteht darin, daß für die unvollkommene Desorpabgewichen und die Desorption zu einem Zeitpunkt i tion nur wenig Spülgas bzw. Energie gebraucht

abgebrochen, welcher in der Nähe des Zeitpunktes liegt, bei dem die Beladung des Spülgases mit dem desorbierten Bestandteil absinkt. Der infolgedessen nur unvollkommen desorbierte Adsorber wird anschließend wieder auf Adsorption geschaltet und möglichst so lange beladen, als er voll annahmefähig ist, um anschließend, nach Umschaltung der Adsorber, erfindungsgemäß wieder der unvollkommenen Desorption unterzogen zu werden.

Es ist ersichtlich, daß beim erindungsgemäßen Verfahren der regenerierte Adsorber unter sonst gleichen Bedingungen seineller wieder betriebsbereit ist als bei vollkommener Desorption. Der besondere Vorteil des erfindungsgemäßen Verfahrens besteht darin, daß für die unvollkommene Desorption und geging Spillegs, bzw. Energie gebraucht

wird wahrend bei der weitergehenden Desorption mach den bekannten Verfahren das erforderliche Spillgasvolumen unch einer Exponentialfunktion, d.h. unverhaltnismäßig stark absteigt oder eine starke Temperaturerhöhung notwendig ist.

Obwood erholungsgemält nur unvollkommen de orblett wir l. hann wahrend des Adsorptionsvorganger is giel he Reinheit (Adsorptionswirkung) ses Gases wie im Anschluß an eine vollkommene

Desorption erreicht werden.

Versuehe linben erwiesen, daß für die vollkommene Reinigung des Gases bei häufig wiederholter Adsorption bereits eine Schichtlänge von 1 m gening. Bei gescherer Schichtlänge kann die Um-

schaltung seltener vorgenommen werden.

Die lekannen, für Adsorption und Desorption angewenderen Hilfsmaßnahmen, wie Kühlung während der Adsorption und Anwarmaung oder Druck senkung, eventuell auch unter Atmos härendruck, während der Desorption u. dgl., können naturlich auch beim erundungsgemällen Verfahren hinzugezogen werden. Die Ersparnis an Spülgas bzw. Energie besteht auch in diesen Fällen. Es ergeben sich somit im wesentlichen folgende Möglichkeiten zur Durchführung des erfindungsgemäßen Ver-

a) Wenn bei der Ad- und Desorption gleiche, und zwar etwa Raumtemperaturen angewendet werden, so genügt es, wenn das Spulgasvolumen das t., 3 bis 2fache des Roligasvolumens beträgt. Dement sprechend kann z. B. bei Gaszerlegungsverfahren ein in den Strott des unter Druck stehenden Rollgases geschalteter Adsorber durch ein gasförmiges entspanntes oder unter Unterdruck abgesaugtes 35 Zerlegungspro ha'd gleicher Temperatur oder durch einen Teil dessellen desorbiert werden. Bei gemigend großen Druckunterschieden kann dann sogur ein Teil des betreffenden Zerlegungsproduktes. welches nicht zum Spülen des Adsorbers gebraucht wird, rein gewonnen werden. Andererseits ist hierbei die Ameleherung des desorbierten Bestandteiles im Spülgas besonders hoch, was für die eventuelle Gewinnung des Bestandteiles günstig ist. Diese Vorteile gelten zum Teil auch für die nachstehenden Möglichkeiten.

b) Wenn für die Desorption eine höhere als die Adsorptions oder Raumtemperatur augewendet wird, so kann das Spülgasvolumen weiter erheblich vermindert werden. Eine Temperaturerhöhung von z. Il. 20 auf 100' ermöglicht eine Herabsetzung des Spallgasvolumens auf Vac bis Vac des Rohgas-

voicinens

er Sind die Gasvolumen bei der Ad- und Desorption aunithernd gleich, so genügt für die Desorption eine Temperaturerhöhung um etwa 5°, vorausgesetzt, daß die Adsorption bei Temperaturen erfolgt, die nicht allzu stark von der Raum

temperatur aby other.

d) Errolgen Ad and Description bei tiefen Tem 60 peratures, z. E. le. 100 oder darunter, so muß wegen der schlechteren Desarptionsmöglichkeit bei , diesen Temperaturen das Spulgasvolumen das 2,5 bis rotache des Rohgasvolumens beträgen. Auch

in silesem Fall eigibt sich eine ethebliche Einsparung an Spülgas im Vergleich zu den Spülgas- 65 mengen, die bei vollkommener Desorption nötig

Nach dem erfindungsgemäßen Verfahren ist es möglich, die Restbeladung des gereinigten Gases für die Dauer auf geringer Höhe zu erhalten. Legt 70 man Wert auf besonders hohe Reinheit, so genügt es, beim erfindungsgemäßen Verfahren nach einer größeren Anzahl von Umschaltungen eine einmalige, stärkere Desorption beider Adsorber unter Anwendung einer größeren Spülgasmenge oder 75 höherer Temperaturen durchzufuliren. Wie bit. diese zusätzliche Desorption erforderlich ist, muß sich nach den jeweiligen Betriebsverhältnissen richten. Es dürfte aber kaum Fälle geben, in denen eine solche zusätzliche Desorption öfter als nach einigen hundert Umschaltungen erforderlich wird, d. h. also, daß solche zusätzlichen Desorptionen in den erwähnten Ausnahmefällen nur in Abständen von mehreren Tagen oder Wochen erforderlich sind.

An Hand der graphischen Darstellungen (Abb. 1 bis 5) wird der Verlauf des Ad- und Desorptionsvorganges bei dem erfindungsgemäßen Verfahren im Vergleich zu den bekannten Verfahren erläutert.

In sämtlichen Abbildungen stellen die Ordinaten die Länge des Adsorbers in Strömungsrichtung und die Abszissen den Beladungsgrad dar, wobei Beladungsgrad 1,0 die maximale Beladungsmöglichkeit bei einer bestimmten Konzentration des zu adsorbierenden Bestandteiles im Gase, also die dem Partialdruck der zu absorbierenden Gaskomponente und der Temperatur entsprechende Sättigung des Adsorbens, bedeutet.

In Abb. 1 stellt die Kurve O.1 die Beladungs front am Schluß einer Adsorptionsperiode dar, wenn das unreine Gas in Pfeilrichtung strömt. Am unteren Ende des Adsorbens herrscht also die Beladung Null oder unter Umständen auch die zu-Easige Beladung (wenn keine vollkommene Entferming des betreffenden Gasbestandteiles beabsichtigt ist), so daß bis zum letzten Zeitpunkt vor der 105 Umschaltung Gas gewünschter Reinheit aus dem Adsorber austritt. Öberhalb des Punktes A ist der Adsorber voll beladen.

Abb. 2 stellt den Zustand am Schluß einer Desorptionsperiode bei dem bekannten Verfahren 110 dar. Der Adsorber ist fast vollständig entladen; am oberen Ende des Adsorbers bei B herrscht meistens noch ein geringer Beladungsgrad E, während der Adsorber bis zur Höhe D vollkommen desorbiert ist, soweit dies durch das verwendete Spülgas mög- 115 lich ist. Die Fläche BDE stellt die Rest eladung dar, die in der Regel gering ist.

Während bei dem erfindungsgemäden Verfahren am Schluß einer Adsorptionsperiode genau wie beim bekannten Verfahren der durch Alde i dag. 120 gestellte Beladung-zustand bestel i wird erin leugeremail die Description nur so innes his die Beladungsfront, die in der Abb. i durch die Kurve O I dargestellt wird, his zur Kurve FC (Abb. 3) zuruckgeschohen ist, wober das Spalgas 125 am oberen Ende aus dem Adsorber noch mit einer

weschaliehen Beladung austritt. Sein Gehalt an dem desorbierten Bestandteil wurde aber auschließend bei Aufwendung entsprechend großer Spalgasmengen oder höherer Temperaturen merklich absinken.

Es kommt bei der Durchführung der Erfindung nicht darauf an, daß dieser Zeitpunkt zur Umschaltung haarscharf erfaht wir l. Es wird sich vielmehr empfehlen, einige Zeit das Spälgas zu analysieren und zu warten, bis sein Gehalt an dem desorbierten Bestandteil absinkt und danach die zweckmaßige Desorptionsdauer bzw. die Umschaltzeit der beiden Adsorber festzulegen, eventuell unter geringer Abkürzung oder Verlängerung des für die unvollkommene Desorption ermittelten Zeitraumes, je machdem, ob auf vollkommene Adsorption oder geringe Umschaltverluste Wert gelegt wird.

Die Fläche OACED, Abb. 4, stellt die Beladung dar, welche bei dem bekannten Verfahren nach jedem Adsorptionsvorgang desorbiert werden muß, während die Fläche OACF, Abb. 5, die Beladung darstellt, welche beim Verfahren nach der Eründung jeweils zu desorbieren ist, wobei die Ersparnis durch die Fläche FCED dargestellt wird. Da nan aber, wie bereits eingangs erläutert, für geringe Beladungsgrade sehr viel mehr Spülgas bzw. Energie zum Abbau gleicher Beladungsmengen aufgewendet werden muß, als bei voller Beladung, so ergibt sich die eingangs erläuterte wesentliche Spülgas bzw. Energiezsparnis beim erfindungsgemäßen Verfahren.

Obwohl das Spülgas aus dem Behälter volibeladen austritt, ist doch, wie der Linienzug FC (Abb. 3 und 5) zeigt, ein großer Teil des betreßenden Adsorbers, soweit dies durch das verwendete Spülgas möglich ist, desorbiert worden, was dadurch erreicht wird, daß dasselbe Spülgas, welches bis zum Schluß aus dem Adsorber praktisch vollbeladen austritt, in denselben am anderen Ende unbeladen eingetreten ist und daher diesen Teil des Adsorbers zu desorbieren vermag.

Abweichungen von den dargestellten Kurven, z. B. innerhalb der Grenzkurven GH und JK

(Abb. 5) können aus betrieblichen Gründen unter Umständen notwendig sein und sind im Rahmen 45 des erfindungsgemäßen Verfahrens zulässig.

#### PATENTANSPRÜCHE:

1. Verfahren zur Entierung oder Gewinnung adsorbierbarer Bestandteile aus strömenden Gasgemischen durch Adsorption und anschließende Desorption, dadurch gekennzeichnet, daß die Desorption zu einem Zeitpunkt abgebrochen wird, welcher in der Nähe des Zeitpunktes liegt, bei dem die Beladting des Spülgases mit dem desorbierten Bestandteil absinkt.

2. Verfahren nach Anspruch i bei Anwendung annähernd gleicher Temperaturen zur Ad- und Desorption, dadurch gekennzeichnet, daß das Spülgasvolumen das 1-, 3- bis 2fache des Rohgasvolumens beträgt.

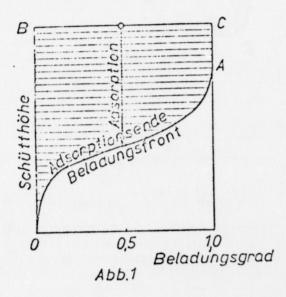
3. Verfahren nach Anspruch i bei Anwendung einer Spülgastemperatur, die annähernd um 80° höher ist als die Adsorptions- oder Raumtemperatur, dadurch gekennzeichnet, daß das Spülgasvolumen 1/30 bis 1/20 des Rohgasvolumens beträgt.

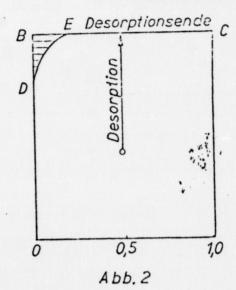
4. Verfahren nach Anspruch i bei Anwendung annähernd gleicher Gasvolumen für Ad- und Desorption, dadurch gekennzeichnet, daß die Desorption bei nur etwa 5° höherer Temperatur erfolgt als die Adsorption.

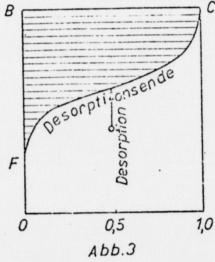
5. Verfahren nach Anspruch i bei Anwendung tiefer Temperaturen bei der Ad- und Desorption, z. B. unter — 100°, dadurch gekennzeichnet, daß das Spülgasvolumen das 2-, 5- bis 10fache des Rohgasvolumens beträgt.

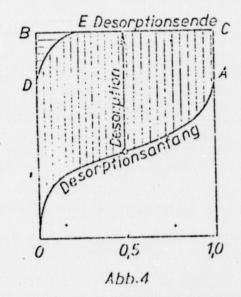
6. Verfahren nach Anspruch 1 bis 5, dadurch gekennzeichnet, daß nach einer größeren Anzahl von Umschaltungen beide Adsorber einer einmaligen, stärkeren Desorption durch Anwendung größerer Spülgasmengen und oder höherer Temperaturen unterzogen werden.

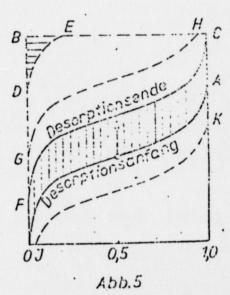
Hierzu I Blatt Zeichnungen











German Patent #871856; Inventor Kahle; Patent Published February 19. 1953 and Issued March 26, 1953

It is known that one can use adsorption processes for the removal or obtaining of mixture components of gas mixtures by using adsorbers which are arranged in pairs and which are periodically switched for the purpose of adsorption and desorption. During desorption through purging with a gas or through evacuating, the gas flow is, as a rule, in the opposite direction of the gas flow during the adsorption process. Up to now, the aim was to desorb the adsorption means (desiceant) to the greatest extent possible prior to the beginning of each adsorption process.

This invention deviates from this rule considerably and desorption is stopped at a point when the loading of the purge gas with the component that is to be desorbed is diminishing. The adsorber, which consequently is only incompletely desorbed, is subsequently switched to adsorption again and is being loaded as long as it is capable to be loaded, and is subsequently, after switching of the adsorber, again desorbed incompletely in accordance with this invention.

It is evident, that in accordance with this invention, everybeing equal, the regenerated adsorber gets back into operation quicker than with complete desorption. The special advantage of the process per this invention is that for the incomplete desorption only little purge gas, respectively energy, is required, while for extensive desorption in accordance with the known processes the required purge gas volume increases exponentially, or a high temperature increase is necessary.

Although the desorbing in accordance with this invention is only incomplete, the same purity of the gas during adsorption can be obtained as after a complete desorption.

Experiments have shown that for the complete purifying of the gas by frequent, repeated adsorption, even a desiceant column of one meter is sufficient. By greater column lengths the switching can take place less frequently.

The usual assists for adcorption and desorption, like cooling during adsorption and heating or pressure reduction, eventually also less than acmospheric pressure, during desorption etc., can of course be utilized in the procedure per this invention. The

savings on purge gas, respectively energy, exist also in these cases. Therefore, the following possibilities essentially exist in executing the process per the invention:

- all furing ad- and desorption the same and approximate ambient temperatures are being utilized, then it is sufficient if the purge gas volume is one, two, or three times the raw gas volume. Accordingly, in the gas fractionation process an adsorber which has been in the stream of raw gas under pressure can be desorbed, by means of a fractionation product or a part of it which is depressurized or was removed by vacuum, at the same temperature. With sufficiently large pressure differential, a part of the fractionation product in question, which is not needed for the purging of the adsorber, can then even be obtained pure. On the other hand, the enrichment with the desorbed component is particularly high in the purge gas, which is an advantage for the eventual obtaining of the component. These advantages are valid in part also for the following possibilities:
- b) If a higher temperature is used for desorption than the adsorption or ambient temperature, then the purge gas volume can be reduced considerably further. For example, a temperature increase from 20 to 100 degrees C. allows a reduction of the purge gas volume to 1/30 to 1/20 of the raw gas volume.
- c) If the gas volumes during adsorption and desorption are approximately the same, then it is sufficient to increase the desorption temperature by approximately 5 degrees, assuming therby that the adsorption takes place at a temperature which does not vary greatly from the ambient temperature.
- d) If the adsorption and desorption take place at low temperatures, for example -100 degrees or lower, then the purge gas volume has to be 2½ to 10 times the raw gas volume on account of the bad desorption conditions at these temperatures. In this case, too, there is a considerable saving on purge gas when compared to the quantity of purge gas required with complete desorption.

In accordance with this invention, it is possible to keep the residual loading of the purified gas very small permanently. If one is concerned with especially high purity, then it is sufficient in this invention to undertake a stronger desorption of both adsorbers by means of a larger purge gas volume or a higher temperature one time after a larger number of cycles. How often this additional desorption is required depends on the respective oper-

ating conditions. However, there hardly should be a case in which such additional desorption is required more frequently than after a few hundred cycles, this means, therefore, that such additional desorption in the exceptional cases is only required at intervals of several days or weeks.

On hand of drawings 1-5 the process of ad- and desorption of this invention is compared with the known process.

In all drawings the ordinate represents the height of the adsorber in the direction of the flow and absissa represents the degree of loading, whereby one is the maximum loading capacity at a certain concentration of the gas component which is to be adsorbed, in other words, representing the corresponding saturation of the desiccant corresponding to the partial pressure of the gas component which is to be adsorbed, and the temperature.

In drawing I the curve OA represents the loading front at the end of an adsorption period, with the unpure gas flowing in the direction of the arrow. Therefore, at the lower end of the desiccant there exists no loading at all or under the circumstances also a parial loading (when it is the intention not to achieve a complete removal of the respective gas component.) So that, therefore, up to the very last moment prior to the cycling, gas of the desired purity can be obtained from the adsorber. Above point A the adsorber is fully loaded.

Drawing 2 shows the situation at the end of the desprption pweriod of the commonly known process. The adsober is almost entirely unloaded. At the upper end of the adsorber at B, there most times is still a small loading E, while the adsorber is completely desorbed up to the height D to the degree that this is possible with the purge gas utilized. The area BDE represents the residual loading which as a rule is small.

While the process at the end of the adsorption period under the commonly known procedure as shown in Drawing #1 is the same as the process described in this invention, the desorption in accordance with this invention is only performed until the loading front, which is shown in Drawing #1 by the curve OA, is pushed back to curve FC in Drawing #3, whereby the purge gas at the upper end of the adsorber leaves with still a substantial loading.

The content of desorbed component would, however, subsequently reduce itself noticeably with utilization of correspondingly larger purge gas volumes or higher temperature.

In the utilization of this invention, it is not critical that the point of switch-over be precisely determined. It is, on the contrary, recommended to analyze for some time the purge gas and wait until its content of desorbed component diminishes and then to establish appropriate desorption time, respectively cycling time of the two adsorbers, eventually with some shortening or lengthening of the time interval for incomplete desorption, depending whether one looks for complete adsorption or small cycling losses.

The area OACED, Drawing 4, represents the loading which per the commonly known process has to be desorbed after each adsorption cycle, while the are OACF, Drawing 5, represents the loading which has to be desorbed per the process of this invention, whereby the saving is represented by the area FCED. As previously explained, for a low degree of loading, much more purge gas, respectively energy, has to be used to remove an equal quantity of lad than is necessary at full loading, therefore, the savings of substantial purge gas, respectively energy, in the process per this invention, is clear as explained above.

Although the purge gas is leaving the container fully loaded as shown in the line FC of drawings 3 and 5, a large part of the respective adsorber has been desorbed, to the extent that this is possible, through the use of the purge gas used. This was acheived because this purge gas, which leaves the adsorber practically fully loaded, entered the adsorber at the other end unloaded, and therefore was able to desorb this part of the adsorber.

Variations from the pictured curves, for example within the limit-curves of GH and JK, Drawing 5, might be necessary for operational reasons and circumstances and are proper within the framework of this invention.

- 1. Process for removal or obtaining of adsorbable components of flowing gas mixtures through adsorption and subsequent desorption characterized by the desorption being broken off at a point which is near the point when the loading of the purge gas with the desorbable component diminishes.
- 2. Process per Claim 1 using approximately the same temperature for ad- and desorption, characterized by the purge gas volume being on, two, three times the raw gas volume.
- 3. Process in accordance with Claim 1 using a purge gas temperature which is about 80 degrees higher than the adsorption for ambient temperature, characterized by the purge gas volume being 1/30-1/20 of the raw gas volume.
- 4. Process per Claim 1 using about the same gas volume for ad- and desorption, characterized by the desorption taking place at only about 5 degrees higher temperature than the adsorption.
- 5. Process per Claim 1 using lower temperatures at adamd desorption, for example, below -100 degrees, characterized by the purge gas volume being two, five, to ten times the raw gas volume.
- 6. Process per Claims 1 through 5 characterized by a stronger desorption by larger purge gas volumes and/or higher temperatures after a greater number of cycles.

# PLAINTIFF'S EXHIBIT 5C

Kahle German Patent No. 882,541 and Translation

Erteilt auf Grund des Ersten Überleitungsgesetzes vom 8. juli 1949 (WIGBL S. 175)

# BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM 9. JULI 1953

**DEUTSCHES PATENTAMT** 

# **PATENTSCHRIFT**

Mr. 882 541 KLASSE 12e GRUPPE 302

. G 6724 IVb/12e

Dipl.-Chem. Tr.-Jug. Heinrich Kahle, Pullach bei München ist als Erfinder genannt worden

. Gesellschaft für Linde's Eismaschinen Aktiengesellschaft, Höllriegelskreuth bei München

Verfahren und Vorrichtung zur Trennung bzw. Reinigung von Gasgemischen

Patentiert im Gebiet der Bundesrepublik Deutschland vom 8. August 1951 an Patentanmeldung bekanntgemacht am 9. Oktober 1952 Patenterteilung bekanntgemacht am 28. Mai 1953

Das nachstehend beschriebene Verfahren betrifft ein verbessertes rationelles Verfahren zur Reinigung bzw. Trennung von Gasgemischen mit wesentlichen Gehalten an adsorbierbaren Gasen oder Dämpfen 5 mittels periodisch umschaltbarer Adsorber. Es ist bei der Zerlegung von Gasgemischen vorgeschlagen worden, daß man durch Zuschalten von Speichern zu Adsorbern mit Heiz- oder Kühleinrichtung für eine Rückgewinnung aufgewendeter Wärme- und 10 Kältebeträge sorgt, d. h. wenn das Spülgas erhitzt und das Adsorbens gekühlt werden mußte. Auf diese Weise war es möglich, die zum Zweck der Adsorption hermtergekühlten Gase und die zum Zweck der Desorption erhitzten Spülgase nach 15 ihrem Austritt aus dem Adsorbens ohne erhebliche Kalorienverluste auf annähernd Normaltemperatur

zu bringen.

baren Gasbestandteilen abhängt. Die Wärmebeträge bei der Adsorptich werden erfindungsgemäß dadurch wieder für die folgende Desorption nutzbar gemacht, daß man an der Austrittsseite des gereinigten durch die frei gewordene

Es hat sich herausgestellt, daß die Verwendung

mäßig ist, wenn Wärme oder Kälte von außen zu- 20

von Wärmeaustauschern nicht nur dann zweck-

oder abgeführt werden muß, sondern auch dann.

wenn durch die Adsorption adsorbierbarer Gas-

bestandteile merkliche Wärmebeträge frei bzw.

durch die Desorption gebunden werden. Ein Gas-

frei werdenden Adsorptionswärme bzw. kühlt es

sich und das Adsorbens infolge der frei werdenden

Desorptionskälte ab, wobei das Ausmaß der Warme-

tönung vom Gehalt des Gasgemisches an adsorbier-

gemisch erhitzt sich und das Adsorbens infolge der 25

#### 882 541

Adsorptionswärme erhitzten Gases für einen Wärmeaustausch sorgt, so, daß das Spülgas, welches für die Desorption Verwendung finden soll, vorgewärmt wird, während das erhitzte durch Adsorption gereinigte Gas abgekühlt und im Austausch mit dem Spülgas wieder rückgekühlt wird. Voraussetzung ist, daß die Spülung stets entgegengesetzt zur Beladung erfolgt und das Adsorbens nicht völlig entladen wird.

Es hat sich ferner herausgestellt, daß auch bei der Desorption nicht unerhebliche Energiebeträge verlorengehen, was besonders dadurch bedingt ist, daß für die Desorpti a, ähnlich wie bei der Verdunstung. Wärme aufgewendet werden muß und diese dem Spülgas entzogen wird, welches infolgedessen aus dem in der Entladung befindlichen

Adsorber unterkühlt austritt.

Es wird daher erfindungsgemäß auch auf der Seite des Frischgaseintrittes für einen Wärmeaustausch des beladenen Spülgases mit dem Frischgas gesorgt.

Auf diese Weise wird das Frischgas im Wärmeaustausch mit dem Spülgas heruntergekühlt und betritt den Adsorber in einem vorgereinigten und

vorgekühlten Zustand.

Die geschilderte Maßnahme ist deshalb besonders wichtig, weil fast alle technischen Gasgemische Wasserdampf enthalten und in den meisten Fällen, besonders wenn sie komprimiert sind, mit Wasser gesättigt ankommen. Durch die beschriebene Vorkühlung wird das Wasser bereits zu einem wesentlichen Teil ausgeschieden. Das Adsorbens kann daher mit anderen wertvollen Gasbestandteilen reichlicher beladen werden und eine Verlängerung der Laufzeit der Adsorber bzw. eine bessere Abscheidung der adsorbierbaren Gasbestandteile ist die Folge.

Die beschriebenen Maßnahmen des Wärmeaustausches hinter bzw. vor den Adsorbern können sowohl jede einzeln als auch beide gleichzeitig angewendet werden, derart, daß die Adsorber zwischen

Wärmeaustauschern angeordnet werden.

Als Wärmeaustauscher können periodisch umschaltbare Regeneratoren verwendet werden, die zweckmäßig mit den Adsorbern ständig kommunizieren, d. h. mit dem Anfang bzw. Ende des Adsorbensraumes ständig verbunden sind und•mit diesem gleichzeitig umgeschaltet werden. In diesem Fall sind also die Adsorbentien zwischen Regeneratoren angeordnet bzw. befinden sich deren Speichermassen und das Adsorbens jeweils in den gleichen Behältern in der beschriebenen Anordnung.

Sollen Gegenstromwärmeaustauscher an Stelle von Regeneratoren verwendet werden, so brauchen die ersten nicht periodisch umgeschaltet und nicht doppel: ausgeführt zu werden. Es genügt vielmehr auf jeder Seite jedes periodisch umgeschalteten Adsorbers ein Gegenstromwärmeaustauscher, der von jeder Gasart ständig in einer bestimmten Richtung durchströmt wird. Die Umschaltungen für die Gasströme sind also im vorliegenden Fall zwischen Genstromwärmeaustauscher und Adsorberpaar, angeordnet. Auch hier kann je nach Zusammen-

setzung des Gasgemisches bzw. Betriebsumständen ein Wärmeaustauscher auf der einen oder auf der anderen Seite des Adsorberpaares oder je ein Wärmeaustauscher gleichzeitig auf beiden Seiten des Adsorberpaares zur Anwendung kommen. In dem auf der Eintrittsseite des Frischgases benndlichen Gegenstromwärmeaustauscher wird zweckmäßig für eine Abscheidungsmöglichkeit für Kondensate gesorgt.

Die Umschaltung der Gasströme von einem Adsorber bzw. Regenerator auf den anderen erfolgt erfindungsgemäß automatisch, was insbesondere deshalb zweckmäßig ist, weil bei Normaltemperatur die adsorbierten Mengen bestimmter nur mäßig adsorbierbarer Gasbetandteile nicht erheblich sind und, wenn diese vollständig entfernt werden sollen, eine kürzere Umschaltzeit erforderlich ist. Andererseits ist mit der Adsorption bei Normaltemperatur eine wesentliche Energieeinsparung verknüpft, so daß kürzere Umschaltzeiten in Kauf genommen

werden können.

Erfolgt die Adsorption unter Druck, die Desorption bei geringerem Druck, so wird kurz vor der Umschaltung Druckausgleich herbeigeführt. Man kann zum Zweck weitgehender Gas- und Zeitersparnis einen Druckausgleich z.B. auf beiden Adsorbensseiten einstellen. Als besonders zweckmäßig erwies sich ein Druckausgleich lediglich auf der Seite des Austrittes des gereinigten Frischgases, da die Störung des Reinigungsprozesses dabei am geringsten war. Notwendig ist ferner eine völlige Druckentlastung im zu entladenden Behälter. Als zweckmäßig erwies sich eine Druckentlastung gegen die Stromrichtung des Frischgases vor Zuleitung des Spülgases zu dem zu entladenden Behälter. Auf diese Weise werden Abscheidungen usw. bereits mechanisch fortgeführt und gelangen 100 nicht in den etwa nachgeschalteten Zerlegungsapparat. Sind die Gehalte an adsorbierbaren Bestandteilen schwankend, so wird zweckmäßig die Umschaltung durch Einbau eines Temperaturfühlers an einer Stelle, die von der durch die Ad- 105 sorption ausgelösten Wärmewelle, z. B. in oder dicht hinter dem Adsorbens, erreicht wird, ge-steuert, derart, daß z. B. bei Überschreitung einer bestimmten Temperatur die Umschaltung ausgelöst

Das erfindungsgemäße Verfahren sei durch zwei Ausführungsbeispiele näher erläutert, wobei

Fig. t den Fall der beidseitigen Verwendung von Regeneratoren,

Fig. 2 den Fall der Verwendung von Gegen 215 stromwärmeaustauschern veranschaulicht.

In der Fig. 1 stellen dar: 1 und 2 die Adsorbensschichten zwischen den Speichermassen 3 und 7 bzw. 4 und 8 auf der anderen Seite. Die Umschaltvorrichtungen 5 und 6 besorgen die periodische Umschaltung der Gasströme. Sie werden automatisch geschaltet. Das Frischgas, z. B. komprimierte Luft, strömt bei 11 im dargestellten Fall ständig zu, geht in der Richtung der ausgezogenen Pfeile über Umschaltung 6, Speichermasse 4, Adsorber 2, Speichermasse 8 und Umschaltung 5 bei, 10

zur Verwendung oder weiteren Zerlegung. Wer der in der Periode vorher gekühlten Speicher-masse 4 wird das Gas vorgekühlt und gibt dabei einen Teilgehalt an kondensierbaren Bestandteilen (Wasserdampf) bei der Speichertemperatur ab, tritt vorgekühlt und vorgereinigt auf das Adsorbens 2, wo es von den adsorbierbaren Bestandteilen (CO2. H2O, C2H2) vollständig befreit wird, gibt die bei der Adsorption frei gewordene Wärme teilweise am Adsorbens 2, teilweile an der Speichermasse 8 ab und strömt anschließend über 5 und 10 gereinigt, getrocknet und gekühlt zur Verwendung. Gleichzeitig wird über 9 ständig trockenes Spülgas, z. B. druckloser Stickstoff, zugeführt und geht im dargestellten Fall über die Umschaltung 5 durch den linken Adsorber in der Richtung der ausgezogenen Pfeile, also über Speichermasse 7, Adsorbens 1 und Speichermasse 3, um über Umschaltung 6 bei 12 in beladenem Zustand auszutreten. Über der in der Periode vorher angewärmten Speichermasce 7 wird das Spülgas dabei vorgewärmt, so daß die Entladung des Adsorbens i erleichtert wird. Das am Ende des Adsorbens bereits wieder infolge Wärmeabgabe an 25 das za entladende Adsorbens und infolge Deckung des Wärmebedarfes bei der Desorption abgekühlte Spülgas wird nunmehr über Speichermasse 3 wieder auf annähernd Normaltemperatur angewärmt, so daß es ohne wesentlichen Kalorienverlust austritt. Nach einer gewissen Zeit ist die Speichermasse 7 und ebenfalls die Speichermasse 3 teilweise so weit gekühlt, daß eine Umschaltung erfolgen muß. Zu diesem Zweck wird zunächst Stickstoffauslaßventil 22 in einer seitlichen Abzweigung kurzzeitig geöffnet, so daß das Spülgas (Stickstoff) vor der Einrichtung ins Freie tritt. Das erwähnte Ventil wird elenso wie die anderen Ventile zweckmäßig automatisch gesteuert. Es wird nur so lange geöffnet, als der Druck im zu spülenden Behälter, der durch Ventil 14 entlastet wird, noch nicht auf den Druck des Spülgases abgesunken ist. Die Umschaltventile 5 und 6 werden für kurze Zeit in Schlußstellung gebracht. Durch Offnen von Ventil 21 werden die Drücke zwischen dem drucklosen und 45 dem unter Druck befindlichen Behälter ausgeglichen und schließlich nach Schließen von 21 der Restdruck im jeweils beladenen Behälter durch die Entlastungsventile 14 (oder 13) gegen die Strömungsrichtung des Beladegases entlastet, wonach dieses Ventil wieder geschlossen wird. Während der kurzen Schließzeit der Ventile 5 und 6 wird das ankommende zeitweise nicht abgenommene Frischgas in einem bei 23 angeschlossenen, nicht gezeichneten Behälter gespeichert und die nachgeschaltete 55 Zerlegungsanlage aus einem ebenfalls nicht dargestellten, bei 24 angeschlossenen Behälter auf der anderen Seite der Reinigungsanlage mit Gas beliefert. Durch Offnung der Umschaltungen 5 und 6 wird der Umschaltvorgang beendet. Hiernach geht nunmehr das bei 11 zugeführte Frischgas bzw. das bei 9 zugeführte Spülgas in der Richtung der gestrichelten Pfeile jeweils durch den anderen Adsorber. Das Frischgas wärmt nunmehr die

Speichermasse 3. das gereinigte Gas, die Speichermasse 7 wieder an, während sich die oben bei Adsorber 1 bereits geschilderten Vorgänge bei der Spülung des zu entladenden Adsorbers 2 wiederholen.

Fig. 2 zeigt den Fall der Verwendung von Gegenstromwärmeaustauschern auf beiden Seiten des Adsorberpaares. Hier sind 1 und 2 die Adsorber, 70 welche zwischen der Umschaltung 5 bzw. 6 bzw. den Gegenströmern 15 bzw. 16 angeordnet sind. Im dargestellten Fall strömt das über 18 ständig zugeführte Frischgas (Luft) unter einem Druck von z. B. 5 atu durch den Gegenstromwärme-austauscher 16, gibt dort kondensierbare Bestandfeile (Wasser) ab und tritt vorgereinigt bzw. vorgetrocknet in die Adsorbensmasse 2 ein, um diese üler Umschaltung 5 (von H2O, CO2 und C2H2) gereinigt zu verlassen und mitgeführte Wärmebeträge im Gegenstromwärmeaustauscher 15 wieder an Spülgas abzugeben. Es tritt bei 20 aus. Das bei 19 drucklos zugeführte Spülgas (Stickstoff) wird im Austauscher 15 mit gereinigtem Frischgas (Luft) vorgewärmt und strömt über Umschaltung 5. dann im dargestellten Fall über Adsorbens 1. welches es regeneriert. Es kühlt sich hierbei ab, gibt nach Austritt aus dem Adsorbens im Gegenstromwärmeaustauscher 16 seinen Kälteinhalt an bei 18 zuströmendes Frischgas ab und wird bei 17 ins Freie geführt. Nach der Umschaltung gehen die Frischgase durch das Adsorbens i und die Spülgase durch das Adsorbens 2. Die Gaswege in den Gegenstromwärmeaustauschern werden nicht geändert. Der Ablauf des Schaltvorganges entspricht dem im 95 Fall 1 bereits geschilderten.

Sämtliche Schaltvorgänge erfolgen zweckmäßig automatisch. Die Öffnungs- bzw. Schließzeiten der Ventile während des Umschaltvorganges betragen zweckmäßig nur wenige Sekunden.

#### PATENTANSPRÜCHE:

1. Verfahren zur Trennung bzw. Reinigung von Gasgemischen mittels periodisch umschaltbarer Absorber, die durch Gegenstromspülung 105 entladen werden, dadurch gekennzeichnet, daß zwecks Verwertung der Adsorptionswärme im zu reinigenden Gas an der Austrittsseite des gereinigten Gases Wärmeaustauscher vorgesehen sind, in denen einerseits das gereinigte 110 Gas abgekühlt und andererseits entgegenströmendes Spülgas für die Desorption vorgewärmt wird, und/oder zwecks Verwertung der Desorptionskälte im beladenen Spülgas an der Austrittsseite desselben bzw. an der Eintritts- 11: seite des zu reinigenden Gases Wärmeaustauscher vorgeschen sind, in denen das Frisch as im Wärmeaustausch mit beladenem Spülgas aus dem Adsorber vorgekühlt wird, bevor es zwecks Reinigung oder Trennung durch Adsorption in 12 den zu beladenden Adsorber eintritt.

 Verfahren nach Anspruch t. dadurch gekennzeichnet, daß ein Värmeaustausch vor und hinter den Adsorbern stattfindet.

3. Verfahren nach Auspruch a und 2, dadurch 12 gekennzeichnet, daß als Wärmeaustauscher

#### 882 541

periodisch umschaltbare Regeneratoren verwendet werden.

4. Verfahren nach Anspruch i bis 3, dadurch gekennzeichnet, daß Anfang und Ende des Adsorbensraumes mit den Regeneratoren ständig kommunizieren und Regeneratoren und Adsorber gleichzeitig umgeschaltet werden.

5. Verfahren nach Anspruch I und 2, dadurch gekennzeichnet, daß vor bzw. hinter jedem periodisch umgeschalteten Adsorberpaar je ein nicht umschaltbarer Gegenstromwärmeaustauscher angeordnet wird.

6. Verfahren nach Anspruch 1 bis 5. dadurch gekennzeichnet, daß die Umschaltungen automatisch erfolgen.

7. Versahren nach Anspruch 1 bis 6, dadurch gekennzeichnet, daß im Zuge des Umschalt-

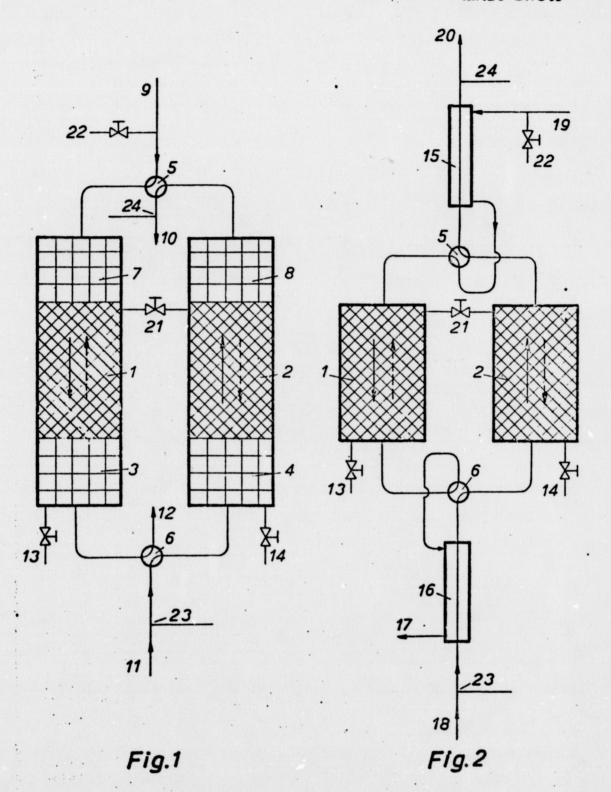
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verfahrens ein Druckausgleich zwischen beladenem und entladenem Adsorbens zweckmäßig auf der Austrittsseite des behandelten Gases sowie schließlich eine Rückentspannung des danach verbließenen Restdruckes gegen die Beladungsrichtung erfolgt.

8. Verfahren nach Anspruch i bis 7, dadurch gekennzeichnet, daß die automatische Umschaltung besonders bei wechselndem Gehalt an adsorbierbaren Bestandteilen durch Temperaturfühler in der Speichermasse oder in dem beladenen Adsorbens gesteuert wird.

9. Vorrichtung zur Ausführung des Verfahrens nach Anspruch 1 bis 8, gekennzeichnet durch Wärmeaustauschvorrichtungen am Ende und/oder Beginn der Adsorbensschicht.

Hierzu I Blatt Zeichnungen



# GERMAN PATENT NO. 882541 KAHLE, LINDE 1951

The following described process concerns an improved rational process for cleaning respectively separation of gaseous mixtures with substantial content of adsorbable gases or vapors by means of periodically cyclable adsorbers. It has been suggested in separation of gaseous mixtures that one provides for the recovery of the expended heat or cold through the addition to the adsorbers of storage with heating or cooling facilities. That means for the heating of the purge gas and for the cooling of the adsorbent in this manner it was possible to bring the for the purpose of adsorption cooled gases and for the purpose of desoprtion heated gases to about ambient temperature after their exit from the adsorbent without considerable calorie loss.

It has been found that the use of heat exchangers is not only practicel when heat or cold has to be added or taken away from outside, but also when noticeable heat quantities are released through the adsorption of adsorbable gas components, respectively are taken on through desorption. A gaseous mixture increases its temperature and that of the adsorbent due to the released adsorption heat, respectively it is cooling itself and the adsorbent due to the released description cold, whereby the degree of temperature shading depends on the amount of adsorbable gas components in the gaseous mixture.

The heat quantity of the adsorption, per this invention, is utilized again for the following desorption in that one urranges for a heat exchange at the exit of the purified and through the released adsorption heat heated gas, so that the purice gas which is to be used for the desorption will be preheated, while the heated

through adsorption purified gas is cooled down and in exchange with the purge gas is again cooled. Presupposed is that the purging always is in counterflow to the loading and that the adsorbent is not fully desorbed.

It has further been found that also during description not inconsequential energy is being lost which is caused by the need for
considerable heat during description, similar to veporization, and
this heat has to be obtained from the purge gas which in consequence
leaves at reduced temperature the adsorber which is being described.

Per this invention therefore, a heat exchange is also arranged on the entrance side of the fresh gas, for heat exchange of the loaded purge gas with the fresh gas.

In this manner the fresh gas temperature is reduced in heat exchange with the purge gas and it enters the edsorber in a procleaned and pre-cooled condition.

The described procedure is particularly important because almost all technical gaseous mixtures contain vater vapor and in most cases, especially when they are compressed, they are saturated with water. Through the described pre-cooling the water is to a considerable degree already separated. The adsorbent therefore can be loaded more substantially with other valuable gas components and an extension of the use of the adsorber, respectively, a better separation of the adsorbable gas components results.

The described procedure of the heat exchange after, respectively ahead of the adsorbers can be applied singly as well as jointly, so that the adsorber is arranged between heat exchangers

As heat exchangers periodic cyclable regenerators can be used which for the purpose are in constant communication with the adsorbers, this means they are constantly connected with the entry,

respectively exit of the adsorbent space and are cycled with it together. In this case, therefore, the adsorbent is arranged between regenerators, respectively the storage masses (of the regenerators) and the adsorbent are in the same containers in the described sequence.

If counterflow heat exchangers are used in place of regenerators, they (the heat exchanger) do not have to be periodically cycled and duplicated. One counterflow heat exchanger on each and of the periodically cycling adsorber is adequate through which each gas type flows constantly in a certain direction. In this case therefore the cycling means for the gas flow is arranged between the counterflow heat exchanger and the adsorber pair. In this case also, depending on the composition of the gaseous mixture, respectively the circumstances of the process, one can use a heat exchanger on one or the other side of the adsorber pair, or a heat exchanger each at the same time on both sides of the adsorber pair. At the counterflow heat exchanger on the entrance side of the fresh gas it would be desirable to arrange for an entrainment separator.

The cycling of the gas streams from one adsorber, respectively regenerator, to the other is automatic per this invention which is especially desirable because at ambient temperature the adsorbed quantities of certain only to a limited degree adsorbable gas components are not substantial, and if these are to be removed entirely a shorter cycling time is needed. On the other hand adsorption at ambient temperature is combined with considerable saving of energy and therefore the shorter cycling times can be tolerated.

If the adsorption takes place under pressure and the desorntion at reduced pressure, shortly before the cycling pressure equalization is arranged. For the purpose of considerable gas and time saving one can arrange for a pressure equalization on both ends of the adsorbent. Particularly practicable was found pressure equalization only on the exit side of the purified fresh gas, because the purifying process was thereby disturbed the least. Furthermore a complete elimination of pressure is necessary in the to be adsorbed container. A pressure release in counterflow to the fresh gas was found expedient prior to the introduction of the purge into the to be desorbed container. In this manner precipitates, etc., are already mechanically removed and do not get into separation apparatus that might be connected downstream. If the content of adsorbable components varies, the cycling would be expediently controlled by means of a temperature sensor at a point that is reached by the heat flow which is released during adsorption, for example, in or close behind the adsorbent, in such a manner that when a certain temperature is exceeded the cycling occurs.

The process per this invention is explained through two examples, whereby figure 1 shows the case of using on both sides regenerators, and figure 2, the case of using counterflow heat exchangers.

In figure 1 are (1) and (2) the layers of adsorbent between the storage masses (3) and (7) respectively (4) and (8) on the other side. The cycling means (5) and (6) provide for the periodic cycling of the gas streams. They cycle automatically. The fresh gas, for example, compressed air flows in constantly at (11) and goes in the direction of the solid arrow via cycling means (6), storage mass (4), adsorber, (2), storage mass (8), and cycling means (5), to the utilization or further separation. In the storage mass (4) which has been cooled during the prior period the gas is pre-cooled and thereby gives off a part of the condensate component (water vapor) at the temperature of the storage, it then enters pre-cooled and propurified the adsorbent (2) where it is cleaned completely of the

adsorbable components (CO2, H2O, C2H2), it gives off in part to adsorbent (2) the released adsorption heat and in part to the storage mass (8) and then flows via (5) and (10) purified, dried and cooled to utilization. Concurrently, dry purge gas flows constantly through (9), for example, pressureless nitrogen, and in the described case flows via cycling means (5) to the left adsorber in the direction of the solid arrows, this means through storage mass (7), adsorbent (1), and storage mass (3) and exits at (12) via cycling means (6) in loaded condition. The purge gas is preheated by storage mass (7), which was preheated during the prior period, so that the desorption of the adsorbent (1) is made ensier. At the end of the adsorbent, due to giving off heat to the adsorbent which is to be desorbed, and having to provide this desorption heat, the cooled purge gas is now again brought up to about ambient temperature by means of storage mass (3), so that it exits without substantial calorie loss. After a certain time storage mass (7) and storage mass (3) are in part cooled down so that cycling has to take place. For this purpose the nitrogen release valve (22) in a branch connection is briefly opened, so that the purge gas (nitrogen) can be released to atmosphere. This valve like the other valves is best automatically controlled. It is opened only for the period of time needed until the pressure in the to be purged container which is being released through valve (14), has sunt to the processor of the purge gas. The cycling valves (5) and (6) are placed in closed position for a short period. Through opening of valve (21) the pressure between the pressureless container and the container under pressure is being equalized and finally after closing of (21) the remaining pressure in the loaded container is released in counterflow to the loading gas, then valve (14) respectively (13), thereafter this valve is closed again. During the short period of closing of valve (5) and (6) the fresh gas is stored in a not shown container which is connected at (23), and the separation apparatus downstream, which is also not shown is supplied with gas from a container connected at (24) at the other side of the purifying apparatus. Through the opening ov valves (5) and (6) the cycling process is concluded. After that the fresh gas coming in at (11), respectively the purge gas, coming in at (9) flow in the direction of the dashed arrows each through the other adsorber. The fresh gas now heats storage mass (3), and the purified gas the storage mass (7), while the above described process with during purging of adsorber (1) repeats itself with the to be described adsorber (2).

Figure 2 shows the case of using counterfice heat exchangers on both sides of the adsorber pair. Here (1) and (2) are adsorbers which are arranged between the cycling means (5) respectively (6), respectively, the counterflow exchangers (15) and (16). In the pictured case the constantly fed fresh gas (air) flows at (18) under pressure, for example (5) atmosphers through the counterflow Component (water) and ent heat exchanger (16), gives off there condensable procleaned, respectively predried the adsorbent mass (2) and leaves it via cycling means (5) cleaned (of H2O, CO2, and C2H2) and gives off the heaf it carries along in the counterflow heat exchanger (15) to the purge gas. It exits at (20). The pressureless purge gas (nitrogen) entering at (19) is proheated with purified frosh dar (air) in exchanger (15) and flows through cycling means (5) to adsorbent (1) which is being regenerated in the illustrated case. Here it cools itself thereby and after leaving the adsorbent it gives off its. cold temperature in counterflow heat exchanger (16) to the at (19) inflowing fresh gas and then exits into the atmosphere at (17). After the cycling the fresh gas goes through adsorbent (1) and the

purge gas through adsorbent (2). The gas flow in the counterflow heat exchangers does not change. The action of the cycling process corresponds to that already described in case 1.

All cycling is best accomplished automatically. The duration of opening respectively closing of the valves during the cycling process advantageously amounts to only a few seconds.

#### Patent Claims

- nixtures by means of periodically cyclable adsorbers, which are desorbed through counterflow purging, characterized in that for the purpose of utilization of the adsorption heat in the to be purified gas a heat exchanger is provided for at the exit side of the purified gas, in which on one hand the purified gas is cooled and on the other hand the counterflowing purpose of utilization of the desorption, and/or for the purpose of utilization of the desorption cooling of the loaded purgo gas a heat exchanger is provided at the exit side of the purgo gas, respectively at the entry side of the to be purified gas, in which the fresh gas is pre-cooled in heat exchange by the from the adsorber coming loaded purgo gas, before it enters the to be loaded adsorber for the purpose of purification or separation through adsorption.
- Process per Claim 1, characterized in that a heat exchange takes place before and after the adsorbers.
- Process per Claims 1 and 2, characterized in that periodically cyclable regenerators are used as heat exchangers.
- 4. Process per Claims 1 through 3, characterized in that the beginning and the end of the adsorption space is in constant communication with the regenerators and the the regenerators and the adsorbers are cycled together.
- 5. Process per Claims 1 and 2, characterized in that before respectively after each periodically cycled adsorber pair a non-cyclable counterflow heat exchanger is arranged.
- 6. Process per Claims 1 through 5, characterized in that the cycling is automatic.

- 7. Process per Claims 1 through 6, characterized in that in the course of cycling a pressure equalization between the loaded and unloaded adsorbent takes place, preferably at the exit side of the process gas, as well as a despressionation of the remainder pressure opposite the direction of the loading.
- 8. A process per Claims 1 through 7, characterized in that the automatic cycling, especially with varying content of adsorbable compenents, is controlled by a temperature sensor in the storage mass or in the leaded adsorbant.
- Apparatus to carry out the process per Claims ! through 8, characterized through heat exchange equipment at the end and/or the beginning of the adsorbent layer.

### PLAINTIFF'S EXHIBIT 5D

Kahle German Patent No. 970,223 and Translation

Erteilt auf Grund des Ersten Überleitungsgesetzet vom 8. Juli 1949 (WICBL S. 175)

#### BUNDESREPUBLIK DEUTSCHLAND



SAUSGEGEBEN AM 28. AUGUST 1958

**DEUTSCHES PATENTAMT** 

## PATENTSCHRIFT

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Dipl.-Chem. Tr. Jug. Heinrich Kahle, Pullach bei München ist als Erfinder genannt worden

Gesellschaft für Linde's Eismaschinen A.-G., Höllriegelskreuth bei München

Verfahren zur Abtrennung adsorbierbarer Bestandteile aus Gasgemischen

Patentiert im Gebiet der Bundesrepublik Deutschland vom 26. November 1948 an
Patentanmeldung bekanntgemacht am 23. Mai 1951
Patenterteilung bekanntgemacht am 14. August 1958

Es ist bekaunt, adsorbierbare Bestandteile von Gasgemischen mittels periodisch umschaltbarer, durch adsorbatfreies Spülgas regenerierbarer Adsorber zufentfernen. Dabei ist es in der Adsorptionstechnik allgemein üblich, daß Adsorbens nur bis zu etwa 50 bis 75% seiner maximalen Aufnahmefähigkeit, die als Gleichgewichtsbeladung bezeichnet wird, zu beladen. Der als Durchbruchsbeladung bezeichnete Wert ist dann erreicht, wenn die Konzentration des zu adsorbierenden Bestandteiles im Endprodukt von einem kleinen konstanten oder nur

wenig sich ändernden Wert plötzlich beschleunigt anzusteigen beginnt.

Das Bestreben geht in der Technik stets dahin, Bedingungen aufzusuchen, bei denen die Aufnahmefähigkeit des Adsorbens gesteigert wird. Dämpfeder Gasbestandteile, deren flüssige Phase auch bei gewöhnlicher Temperatur existiert, wie die Plampfe von Wasser oder organischen Lösungsmitteln, werden bereits bei gewöhnlicher Temperatur darch Adsorptionsmittel, wie Gel, so leicht adsorbiert, daß man in der Nähe ihres Taupunktes je nach Schicht-



länge Durchbruchsbeladungen zwischen 55 und So", a der Sättigungsbeladung von 35 Gewichtsprozent, d.h. eine Gesamtbeladung von etwa 20 Gewichts prozent, erzielt. Benzol wird umer ähnlichen Bedingungen und in ähnlicher Größenordnung von Aktivkohle adsorliert. Anders liegen die Verhältnisse, wenn man versucla, tiefsiedende Gase, wie z.B. die Kohlensäure der atmosphärischen Luit. durch Adsorption weit unterhalb ihrer Taupunktskonzentratien zu entfernen. Bei dem Partialdruck der in der Luft befindlichen Kohlensäure, nämlich 0,2 mm Hg, erzielt man bei gewöhnlicher Temperatur nur eine Gleichgewichtsbeladung von etwa 0.32 cem CO<sub>a</sub>/g Kohle = ~ 0.06 % des Kohlegewichtes. Sucht man etwa die Luft durch Adsorption über Kohle zu reinigen und in der üblichen Weise letztere etwa bis zur Hälfte dieses Gleichgewichtswertes zu beladen, so kommt man trazdem zu keiner genügenden Reinigung. Wie Versuche zeigten. ist erst bei einer wesentlich kleineren Beladung, die bei etwa 0.07 ccm/g Adsorbens = 22 % der Gleichgewichtsbeladung liegt, die Entfernung der Kohlensäure aus dem Gas bis zu einem verlangten Reinigungseffekt von etwa 99% ausreichend. (Bei geringeren Anforderungen an den Reinigungseffekt können höhere Beladungen zugelassen werden.) Nach den normalen Gesichtspunkten in der Adsorptionstechnik erscheint es also zunächst aussichtslos. unter diesen Bedingungen an eine technisch weitgehende Entfernung tiefsiedender Gase auf diesem Wege zu denken, da untragbar hohe Adsorbensmengen aufgewendet werden müßten. Eine wesentliche Verkürzung der Umschaltzeiten (um Adsorbens zu sparen) stößt auf die Schwierigkeit, daß bei der Desorption die bisher übliche Erwärmung und Wiederabkühlung des Adsorbens auf die Adsorptionstemperatur nicht in genügend kurzer Zeit durchgeführt werden kann, zumal da gerade das Adsorbat, das in kleiner Konzentration auf dem Adsorbens sitzt, schwierig zu entfernen ist.

Uberraschenderweise wurde jedoch durch Versuche gefunden, daß die Regenerierung, auch bei kleinen Beladungen, in kurzer Zeit möglich ist, wenn man bestimmte Bedingungen einhält. So war es möglich, mit einem dauernd extrem hohen Reinigungseffekt von 99 % auch kleinste Mengen tiefsiedender (asc. wie CO<sub>2</sub>, bei gewöhnlichem Druck und gewöhnlicher Temperatur aus Gasgemischen, wie Luft, praktisch vollständig zu entfernen, wenn man das Adsorbens, ausgehend von einer Restbeladung, nur bis zu etwa 20 bis 25 % seiner Gleichgewichtsbeladung mit dem abzuscheidenden Gas, wie CO<sub>2</sub>, belädt und bereits vor Erreichung des Durchbruchs den zugeladenen Betrag bei gleicher Temperatur mit überschüssigem Spülgas wieder entfernt.

Wie die Versuche weiter zeigten, waren 10 Minuten ausreichend, um den zugeladenen Betrag ohne Temperaturerböhung, also bei der gleichen Temperatur mit etwa dem Drei- bis Vierfachen des effektiven Rolgasvolumens an Spulgas zu entfernen. Unter Effektivvolumen ist das tatsächlich vom Gas eingenommene Volumen zu verstehen, das sich bei gleichem Gasgewicht etwa amgekehrt proportional zum

Druck ändert. Die verbliebene Restbeladung Letrug unter diesen Verhältnissen etwa 8 %, die jeweils zugeladene Menge etwa 14% des Gleichgewichtswertes. Sie wird im folgenden als Zubahung gekennzeichnet. Weitere länger dauernde Versuche zeigten, daß der gleiche Reinigungseffekt auf die Dauer aufrechterhalten werden konnte und daß für andere 70 Gase ähnlicher Eigenschaften ähnliche Verhältnisse bestehen. Für eine weitgehende Reinigung ist wichtig, daß die Zuladung auch nicht bis zum Durchbruch der abzuscheidenden Komponente erfolgt. sondern bei höchstens 90 % der Durchbruchsbeladung abgebrochen wird. Auf diese Weise bleibt eine genügende Schicht völlig unbeladenen Adsorbens erhalten, welche den äußerst hohen Reinigungseffekt vor Erreichung des Durchbruchs bedingt.

Das Wesen des vorliegenden erfindungsgemäßen 80 Verfahrens zur Abtrennung adsorbierbarer Bestandteile aus Gasgemischen mittels periodisch wechselbarer Adsorber durch adsorbatfreies Spülgas besteht also darin, daß man das Adsorbens nur bis zu einem unter 50 % seiner Gleichgewichtsbeladung sowie unter 90 % seiner Durchbruchsbeladung liegenden Wert auflädt und dann auf den zweiten, inzwischen von der Zuladung befreiten (teilentladenen) Behälter umschaltet, wobei Umschaltzeiten zwischen 5 und 30 Minuten angewendet werden. Bei 90 etwa Atmosphärendruck bewegt man sich in der Nähe der unteren Grenze für die Umschaltzeit, bei erhöhtem Druck in der Nähe der oberen Grenze von etwa 30 Minuten, da mit erhöhtem Druck auch die Aufnahmefähigkeit des Adsorbens steigt. Desgleichen wird bei erstrebtem hohem Reinigungseffekt die Umschaltzeit mehr der unteren Grenze genähert. Diese kleinen Umschaltzeiten werden angewendet. um die Menge des Adsorbens bis zu einem wirtschaftlich noch tragbaren Wert herabzusetzen. Die 100 erfindungsgemäße untere Grenze der Umschaltzeit wird man dabei jedoch nicht unterschreiten können, da das Trägergas für die Verunreinigungen, das meist rein gewonnen bzw. verarbeitet werden soll. teilweise mitadsorbiert wird und dieser Teil bei der 105 nachfolgenden Spülung verlorengeht.

Es ist zwar bereits vorgeschlagen worden, kürzere Umschaltzeiten zu verwenden, die z.B. unter einer halben Stunde liegen können, wie es z. B. die deutsche Patentschrift 624912 im Anspruch 5 vor- 110 schreibt. Dieses Verfahren arbeitet jedoch insofern anders, als die Verkürzung der Umschaltdauer nicht etwa wegen der Absicht, die Beladungshöhe des Adsorbens zu verringern, variiert warde, sondern wegen der Notwendigkeit, die Verweilzeit der auf dem 115 Adsorbens sitzenden, neben Benzol abgeschiedenen polymerisierenden Verunreinigungen zu verkürzen. die das Adsorbens unbrauchbar machen. Das Adsorbens wird daher stärker belastet und das Gas mit größerer Geschwindigkeit hindurchgeführt. Dies 120 soll nach Anspruch i der Patentschrift dadurch erreicht werden, daß »die Adsorbensmenge im Verhältnis zu der, aus den pro Tag zu verarbeitenden Gasen gewinnbaren Kohlenwasserstoffmenge geringer als 2:1 gehalten wirds. Im Gegensatz zum er- 125 findungsgemäßen Verfahren wird also die Be-

lastung des Adsorbens erhöht. Die Desorption erfolgt durch gleichzeitiges in lirele .- Heizen und Ausdämpfen, also praktisch vollstandig und nicht teilweise, wie nach dem erfindungsgemäßen Verfahren, sowie durch Anwendung von unkondensierbaren Spülgasen. Auch wird die maximale Beladung nicht auf höchstens 90 % der Durchbruchs-

beladung beschränkt.

Es ist ferner ein anderes Verfahren nach Patent 704 073 mit kurzfristiger Umschaltung vor Erreichung des Adsorptionsgleichgewichtes angegeben worden, bei dem aber nur eine lediglich wasserstoffreiche (also noch Kohlenoxyd enthaltende) Fraktion aus einem Kohlendioxyd-Wasserstoff-Gemisch gewonnen wird. Es wird also hierbei kein Wert darauf gelegt, daß die Beladung des Adsorbens mit dem zu entfernenden Gasbestandteil auf höchstens 90 % der Darchbruchsbeladung beschränkt wird.

Erfindungsgemäß wird durch diese Maßnahme gewährleistet, daß, wie bereits erwähnt, eine genügende Schicht Adsorbens von Adsorbat völlig frei gehalten wird und das austretende Gas frei ist von der zu adsorbierenden Gaskomponente. Die Tatsache, daß durch das erfindungsgemäße Verfahren auch noch eine hohe Reinheit der behandelten Gase ermöglicht wird, ist um so überraschender, als auf hohe Desorptionstemperaturen verzichtet und das Adsorbens bei gleicher oder nur wenig höherer Temperatur nur teilweise entladen wird.

Der Reinigungesfiekt ist ein besonders hoher, wenn bei der Teilentladung das adsorbatfreie reine Spülgas entgegengesetzt zur Rohgasrichtung durch das Adsorbens strömt. Dabei wird das Spülgas so gut ausgenutzt, daß erfindungsgemäß bereits ein Spülgasvolumen gleich dem Drei- bis Vierfachen des Rohgasvolumens ausreicht, um bei Umgebungstemperatur sowie bei der gleichen Temperatur das Adsorbat so weit zu entladen, daß ein gleichbleibender Reinigungsefiekt von mehr als 99 % für die Dauer gewährleistet wird, ohne daß Spülgas über die Rohgastemperatur angewärmt werden muß. Das Verfahren kann prinzipiell mit allen Adsorbensarten durchgeführt werden. Es ist aber zweckmäßig, mit Adsorbentien besonders hohen Adsorptionsvermögens zu arbeiten und erfindungsgemäß bevorzugt mit solchen, die auf Grund der selektiven Adsorption der abzuscheidenden Bestandteile diese besonders stark zu binden vermögen, während das Trägergas relativ weniger leicht adsorbiert wird. Desgleichen wurde ein großer Einfluß der Körnung des Adsorbensmaterials in dem Sinne gefunden, daß mit feinerer Körnung der Wirkungsgrad der Reinigung steigt. Dieses ist zwar qualitativ theoretisch vorauszusehen, es ist jedoch zweckmäßig, mit Rücksicht auf die Gefahr des Mitreißens bei sehr kleiner Körnung und auf den hohen Druckabfall, der infolge des bei Verwendung von feiner Körnung steigenden Wirkungsgrades entsteht, keine übermäßig

kleine Körnung, sondern nach einem weiteren Erfindungsgedanken Körmingen von 1 bis 2 mm anzuwenden, da es in diesem Bereich noch möglich ist, mit erträglichen Druckabfällen zu arbeiten, besonders wenn dabei erfindungsgemäß Querschnitte der

Adsorbensschicht zwischen 0.5 und 1 qui pro 1000 chm stündlich strömendes Gas angewendet 65 werden. Die Adsorbensschicht soll dabei mit Rücksicht auf den erstrebten hohen Reinigungseffekt mindestens 6.5 in lang - in. Die obere Grenze dieses Wertes richtet sich mach dem zulässigen Dryckabfall und dem mit Rücksicht auf die Mitadsorption 70 des Trägergases begrenzten Aufwand an Adsorbensmenge.

Steht das Gas unter Druck, wobei das Effektivvolumen des verdichteten Gases dem Druck umgekehrt proportional ist, so ist nach einem weiteren 75 Erfindungsgedanken das Volumverhältnis 1:3 bis 4 zwischen Rohgas und Spülgas gewährleistet, wenn der Druck des Rohgases mindestens drei- bis viermal höher ist als der des Spülgases. Ist also z. B. das Normalvolumen, gemessen bei 1 ata, von Roh- 80 gas und Spülgas gleich und der Spülgasdruck = 1.1 ata, so reicht ein Rohgasdruck von 3.3 bis 4,4 ata aus, um dem nach obigem vorgeschriebenen Verhältnis 1:3 bis 4 als unterer Grenze zu genügen. Ist der Reinheitsgrad nicht ausreichend, so kann 85 durch Erhöhung dieses Verhältnisses oder, wenn dies nicht möglich ist, durch Verkürzung der Umschaltzeit in den obigen Grenzen eine Verbesserung erreicht werden, sofern der Verlust an Trägergas noch erträglich ist.

Reicht die zur Verfügung stehende Spülgasmenge nicht aus, so genügt eine Anwärmung um wenige Grade, um unter den gegebenen Bedingungen mit noch kleineren Spülgasmengen auszukommen. Für je eine Halbierung der Verhältniszahl 3 95 ist eine Erhöhung des mittleren Temperaturniveaus der Teilentladung von 3 ° C (untere Grenze) gegenüber dem Zuladungsvorgang ausreichend. Durch diese rationelle Ausnutzung des Spülgases und durch den Wegfall von großen Energien zu seiner 100 Vorerhitzung wird der Umstand aufgewogen, daß die Adsorbensmenge infolge ihrer geringen Beladung immerhin noch relativ groß sein muß. Andererseits ist der Umstand günstig, daß infolge der dabei anzuwendenden größeren Querschnitte der 105 Adsorber der Druckverlust des strömenden Gases kleiner und der Energieaufwand zur Überwindung des Strömungswiderstandes geringer ist. Das allgemeine Temperaturniveau der Beladung und Entladung kann je nach Umgebungstemperatur höher 110 oder tiefer sein. Durch Verkürzung oder Verlängerung der Umschaltzeiten wird man sich den veränderten Bedingungen anpassen können, ohne wesentliche Änderungen an dem Verhältnis von Spülgas zu Rohgasmenge vornehmen zu müssen. 115 Man kann auch, um mit wesentlich kleineren Adsorbensmengen auskommen zu können, erfindungsgemäß bei ticierem Temperaturniveau arbeiten als es die Umgebung aufweist, insbesondere wenn ohnehin das Rohgas aus Gründen der weiteren Zer- 120

legurg abgekühlt werden muß. 1st die Konzentration des abzuscheidenden Bestandteils hoch, so kann man in an sich bekannter Weise zur Abführung der Adsorptionswärme die beiden Adsorber nach Art von Wärmeaustauschern 125 incinander bauen. Die Adsorptionswärme kommt

#### 970 223

dabei dem Entladevorgang, die Desorptionskälte dem Beladevorgang zugute.

Ein Wärmeaustausch zwischen beiden Vorgängen ist auch durch die an sich bekannte Nachschaltung von Speichermassen möglich, an welche die austretenden Rohgase ihre Wärme abgeben. Diese wird ihrerseits nach Umschaltung auf das Spülgas übertragen. Das gleiche Mittel kann augewendet werden, wenn das Spülgas von vornherein kälter ist

als das Rohgas.

Die bei der Adsorption größerer Dampf- oder Gasmengen frei werdende Adsorptionswärme, die dem zu beladenden Adsorbens eine höhere Temperatur erteilt, kann erfindungsgemäß so ausgenutzt werden, daß bereits dann umgeschaltet wird, wenn cine bestimmte Temperaturerhöhung an einer Meßstelle, z. B. in der Mitte des gerade in der Beladung befindlichen Adsorbens erreicht wird. Auf diese Weise bleibt auch die Temperaturerhöhung des Adsorbens zur Förderung der nachfolgenden Teilentladung erhalten. Es ist besonders zweckmäßig, die Temperaturerhöhung dazu auszunutzen, daß man in an sich bekannter Weise diesen Adsorber automatisch nach Auslösung einer dementsprechenden Vorrichtung umschaltet. Dies kann z. B. dadurch geschehen, daß ein Kontaktthermometer bekannter

Art in das Adsorbens eingebaut wird und relaisartig einen Stromkreis schließt, in dem die Um-

schaltvorrichtung liegt.

Das Verfahren sei an einem Beispiel näher erläutert: Luft mit 0,03 % Kohlensäure wird bei 1,4 ata und gewöhnlicher Temperatur über einen von zwei parallel geschalteten Adsorbern, die mit einer Aktivkohleschicht von 1.5 m Länge gefüllt sind, mit einer Raumgeschwindigkeit von 600 cbm pro chm Adsorbens und Stunde geführt. Nach 10 Minuten Beladungszeit werden die Adsorber in bekannter Weise gewechselt und anschließend daran der beladene Adsorber mit kohlensäurefreiem Stickstoff von 1,15 ata bei gleicher Temperatur und mit einer Raumgeschwindigkeit von 2400 cbm pro cbm Adsorbens und Stunde gespült, während der während der Beladung des ersten Adsorbers inzwischen gespülte, teilweise entladene zweite Adsorber beladen wird. Der Reinigungsefickt beträgt nach 100 Stunden Wechselbetrieb 99.5 % entsprechend

0.00015 % Kohlensäure im Endgas.

Die erreichten Vorteile liegen, wie das Beispiel zeigt, in der hohen Reinigungswirkung des Adsorbens, das im vorliegenden Fall nur mit 20 % seines Gleichgewichtswertes, nämlich mit 0.07 cm3 CO./g Kohle beladen ist, ohne daß jedoch infolge der kurzen Umschaltzeit die Adsorber unwirtschaftlich große Ausmaße erhalten. Bei höheren Gehalten au Adsorbierbarem im Rohgas liegt ein besonderer Vorteil darin, daß infolge der kurzen Umschaltzeit praktisch die gesamte Wärme des Adsorptionsvorganges im Adsorber verbleibt und somit für die auschließende Desorption mazbar verwendet wird. Es ist somit möglich, die Entfernung von dampfförmigen Verunreinigungen aus Gasen, die man sonst gern bei höheren Drucken durchführt (wegen des geringeren relativen Dampfgehaltes) ohne Nackteil

für die Reinigungswirkung und mit geringerem Energicantward auch bei niedrigerem Druck durch- 65 zuführen.

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#### PATENTANSPROCHE:

1. Verfahren zur Abtrennung adsorbierbarer Bestandteile aus Gasgemischen mittels periodisch wechselbarer, durch adsorbatfreies Spülgas teilweise regenerierter Adsorbentien, dadurch gekennzeichnet, daß man das Adsorbens nur bis zu einem unter 50% seiner Gleichgewichtsbeladung und unter 90 % seiner Durchbruchsbeladung liegenden Wert auflädt, dann auf den zweiten inzwischen teilweise regene- 80 rierten Behälter umschaltet, während der erste mit überschüssigem Spülgas in entgegengesetzter Richtung teilentladen wird, wobei Umschaltzeiten zwischen 5 und 30 Minuten angewendet werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man die Teilbeladung bei Umgebungstemperatur sowie bei der gleichen Temperatar durchführt wie die Teilentladung und dabei ein Spülgasvolumen gleich dem drei- bis 90 vierfachen effektiven Rohgasvolumen durch das

Adsorbens schickt.

3. Verfahren nach Anspruch 1 und 2, dadurch gekennzeichnet, daß man Adsorbentien hoher selektiver Aufnahmefähigkeit für den abzuschei- 95 denden Bestandteil anwendet.

4. Verfahren nach Auspruch 1 bis 3, dadurch gekennzeichnet, daß man Adsorbenskörnungen

zwischen 1 und 2 mm verwendet.

5. Verfahren nach Anspruch 1 bis 4, dadurch 100 gekennzeichnet, daß man Querschnitte der Adsorbensschicht von 0,5 bis 1 qm pro 1000 cbm stündlich strömendes Gas bei Schichtlängen von mindestens 1,5 m verwendet.

6. Verfahren nach Anspruch 1 bis 5, dadurch 105 gekennzeichnet, daß man bei gleichem Normalvolumen von Rohgas und Spälgas den Druck des Rohgases bei der Beladung drei- bis viermal höher einstellt als den Druck des Spülgases.

7. Verfahren nach Auspruch 1 bis 5, dadurch 110 gekennzeichnet, daß man bei einem Unterschrei ten des Volumverhältnisses Rohgas : Spülgas von 1:3 bis 4 für je eine Halbierung des Verhältnisses eine um 3 Grad höhere Temperatur (untere Grenze) des Spülgases verwendet.

8. Verfahren nach Anspruch 1 bis 7. dadurch gekennzeichnet, daß man das Temperaturniveau der Adsorption und Desorption gegenüber der

Umgebungstemperatur senkt.

9. Verfahren nach Anspruch 1 bis 5. dadurch 120 gekennzeichnet, daß man in an sich bekanater Weise im Interesse eines Wärmeaustausches zwischen Beladungs- und Entladungsvorgang (bei höheren Konzentrationen der abzuscheiden den Bestandteile) beide Adsorber nach Art von 125 Wärmeaustauschern ineinander baut und auf

diese Weise in thermischen Kontakt miteinander bringt.

10. Verfahren nach Anspruch 1 bis 9, dadurch gekennzeichnet, daß man die Adsorber automatisch umschaltet, sobald infolge größerer adsorten Meßstelle im beladenen Adsorbens erreicht ist.

In Betracht gezogene Druckschriften: Deutsche Patentschriften Nr. 624912, 704073: bierter Gas- und Dampfmengen eine vorbe-stimmte Temperaturerhöhung an einer bestimm- Dämpfen«, 1944. S. 107, 108, 121.

#### GERMAN PATENT NO. 970223

It is known that adsorbable components of gas four mixtures can be separated by means of adsorbate-free purge gas through cyclically switchable regenerable adsorbers. It is common practice in the adsorption technique to load the adsorbent only to about 50 to 75 percent of its maximum capacity which is called "equilibrium load." The value which is called "breakthrough load" is then reached when the concentration of the to be adsorbed component increases suddenly in the end product from a small constant or only minimally changing value.

In the technique, efforts are being made constantly to find conditions which increase the capacity of the adsorbent. The vapors of gas components, whose liquid phase also exists at normal temperatures like the vapors or water of organic solvents, are adsorbed so readily at normal temperatures by adsorbents like silica gel, that in promity of their dewpoint and depending on length of layer, breakthrough loads between 55 and 80 percent of saturation load of 35 weight percent, this means a total load of about 20 weight percent is obtained. The conditions are different when one tries to adsorb gases of low boiling point through adsorption far below their devipoint concentration like the CO<sub>2</sub> of the atmospheric air. With the partial pressure of the CO<sub>2</sub> contained in the air, i. e., 0.2 mm of mercury, one obtains at normal temperatures only an equilibrium loading of approximately 0.32 cmm of CO<sub>2</sub> per gram of charcoal. This is approximately 0.06 percent of the charcoal weight. When one tries to purify the air

through adsorption over charcoal and as is customary, tries to load the charcoal up to half of its equilibrium value, one nevertheless does not obtain adequate purification. As tests have shown only by a substantially smaller loading, approximately 0.07 ccm per gram of adsorbent which is approximately 22 percent of the equilibrium loading, does one obtain adequate removal of the CO2 from the gas to a desired purity of about 99 percent. (When lesser requirements of purity exist, higher loading is permissible.) Based on normal considerations in the adsorption technique, it appears hopeless, under these conditions, to think of technically extensive removal of low boiling point gases in this manner because, impractical, large quantities of adsorbent would have to be used. A substantial shortening of the cycle time to save on adsorbent, encounters difficulty in that, during desorption, the up-to-now common heating and cooling of the adsorbent to the adsorbing temperature cannot be accomplished in short enough time, especially as the adsorbate which sits in a light concentration on the adsorbent is difficult to remove.

Surprisingly, however, experiments have shown, that the regeneration, even in the case of small loadings, is possible in a short time interval when certain conditions are observed so it was possible with a constant, extremely high purifying effect of 99 percent to practically remove entirely also smaller quantities of low boiling gases, like CO<sub>2</sub>, at normal pressures and normal temperatures from gaseous mixtures, like air, when the advancent, starting with a residual load, was only loaded up to about 20 to 25 percent of its equal brium load with the gas to be adsorbed like CO<sub>2</sub>, and already prior to the breakthrough being reached the added load was removed at the same temper, tore was

unneeded purge gas.

. As experiments showed, further, ten minutes were sufficient to remove the added load without raising the temperature, in other words, at the same temperature, by means of a purge gas volume which was three to four times the effective raw gas volume. Effective volume should be understood to mean the actual volume occupied by the gas, which is inversely proportional to the pressure of the gas of the same weight. Under these conditions, the residual load amounted to 8 percent and the added load each time to approximately 14 percent of the equilibrium value. In the following, we will use the term of "add-load" for identification. Further experiments of longer duration showed that the same degree of purity could be maintained permanently/for other gases of similar characteristics, similar conditions exist. For effective purifying it is important that the add-load is not increased to the breakthrough point of the component which is to be separated, but is stopped at the latest when 90 percent of the breakthrough load has been reached. In this manner, a sufficient layer of un-loaded adsorbent remains which is a condition for the high purity effect one obtains prior to reaching the breakthrough.

The essential of the foregoing invention to separate adsorbable components from gaseous mixtures by means of periodically cycling adsorbers through adsorbate-free purge gas is that the adsorbent is being loaded at less than 50 percent of its equilibrium load and less than 90 percent of its breakthrough load, and that one then switches ever to a second container which has in the meantime been freed of its add-load (partially un-loaded), whereby a switching cycle of between

five and thirty minutes is utilized. Near atmospheric pressure, one would operate in the area of the lower limit of the cycle time and at higher pressure in the area of the upper limit of approximately thirty minutes because with increased pressure the adsorbing capacity of the adsorbent increases. Likewise, when one is aiming at high purity, the cycle time is to be near the lower limit. These short cycle times are being utilized in order to keep the quantities of the adsorbent economically practical. The lower limit of the cycle time given in this invention will hardly be possible to undercut, because the carrier of gas of the impurities which mostly is to obtained pure, respectively is to be utilized will be in part, also adsorbed and this part will be lost during the subsequent purging.

Admittedly, it has already been suggested to use shorter cycle times which would be less than half an hour and as for example given in patent—o. 624912, i.e. Claim No. 5. This process, however, works differently in that the shortening of the cycle time did not intend to reduce the loading of the adsorbent, but was needed to reduce the duration of time during which the, in addition to the Benzol, separated polymerized impurities, which make the adsorbent unusable, were sitting on the adsorbent. The adsorbent is therefore being I aded heavier and the gas is passed through at higher speed. In accordance with Page I of that patent, this supposedly is being achieved though "the quantity of adsorbent is kept in a ratio of less than 2:1 to the CO<sub>2</sub> quantity obtainable per day. Gontrary to the invention, here, the loading of the adsorbent is increased. The desorption is accomplished through concurrent heating and vaporizing; therefore,

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practically complete and not partial, like in this invention as well as through the use of uncondensable purge gas. Also, the maximum loading is not limited to 90 percent of the breakthrough load.

There is furthermore another process per patent 704073 disclosed with short cycle prior to obtaining of adsorption equilibrium where, however, only a hydrogen rich fraction (therefore still containing CO<sub>2</sub>) is being obtained out of the CO<sub>2</sub> hydrogen mixture. No attention was given to limiting the loading of the adsorbent to a maximum of 90 percent of the breakthrough load.

Per invention as mentioned, already, through this requirement (by limiting the adsorption to a maximum of 90 percent of the breakthrough loading) is assured that a sufficient layer of adsorbent remains entirely free of the adsorbate and the effluent gas is free of the gas component which is to be adsorbed. The fact that through this invention it is possible to obtain high purity of the process gas is still more surprising in view of the fact that high desorption temperatures are not being used and the adsorbent is only partially unloaded at the same or only slightly higher temperature.

The purifying effect is especially high when, during the partial unloading, the adsorbate-free pure purge gas flows in opposite direction to the raw gas flow through the adsorbent. In this manner, the purge gas is so thoroughly used that per this invention, even a purge gas volume of three to four times that of raw gas volume is sufficient to unload the adsorbent at ambient temperature as well as at the same temperature, so that a constant purifying effect of better than 99 percent is guaranteed permanently without that the purge gas has to be heated above the

temperature of raw gas. The process can in principle, be used in all types of adsorbents. However, it is advantageous to work with adsorbent materials that have a specially high adsorption capacity and in accordance with this invention, preferably with those that, through selective adsorption of the component which is to be separated, can bind this component strongly and will adsorb relatively /little of the carrier gas. In this sense, it was found that the particle size of the adsorbent material has considerable influence in that, by smaller size, the effectiveness of the purifying increases. This is to be expected, but it is for practical reasons desirable to avoid excessively small size, to avoid the danger of carrying along the very small particals and getting also a high pressure drop. In the sense of this invention, partical size of one to two mm should be used because in this range it is still possible to have a tolerable pressure drop especially if the cross section of the adsorbent material is between one-half and one qm per thousand chm hourly gas flow. The adsorbent layer should be at least one and one half meter long considering the high purity effect desired. The upper limit of this value depends on the allowable pressure drop and the amount of adsorbent in consideration of the incidental adsorption of the carrier gas.

If the gas is under pressure, whereby the effective volume of the gas under pressure is inversely proportional to the pressure, then in accordance with an additional thought of this invention, the volume relationship of 1:3-4 between raw gas and purge gas is assured when the pressure of the raw gas is at least three to four times higher than that of the purge gas. So, for example, if the standard volume, measuredal, aneata., of raw gas and purge gas is the same, and the purge gas pressure is 1.1 ata., then a raw gas pressure of 3.3 to 4.4 ata, is sufficient

for the above-described relationship of 1:3-4 lower limit. If the degree of purity is not adequate, improvement can be obtained by increasing this ratio, or if this is not possible, through shortening of the cycle within the limits above, /so long as the loss of the carrier gas is still tolerable.

Should there not be enough purge gas available, then heating by a few degrees makes it possible under the given conditions to get away with still less purge gas. Halving the ratio of 3 would require an increase by 3 degrees C (lower limit) of the mean temperature level during the unloading as compared with the on-loading. Through this effective utilization of the purge gas and the doing away with large energy requirements to preheat it, one is compensating for the fact that the adsorbent quantity required has to be relatively large in consideration of its low loading. On the other hand, there is an advantage due to the large cross section of the adsorbent material/the pressure drop of the gas is smaller and the energy required to overcome the pressure drop is smaller. The general temperature level of the onloading and off-loading can vary with the ambient temperauter lower or higher. By shortening or lengthening the cycle, one can adjust to the varying conditions without any substantial changes required in the ratio of purge gas to raw gas. In order to work with considerably smaller adsorbent quantities, one can, in accordance with this invention, operate at lower temperature levels than ambient temperature, especially if the raw gas has to be cooleanyway for reasons of further fractionating.

If the concentration of the component which is to be split off is high, one can build the adsorber towers into each other for the purposes of heat exchange.

The adsorption heat then becomes an advantage in the off-loading process and desorption cooling becomes an advantage in the on-loading.

The heat exchange between the two processes would also be possible through a heat sink arrangement to which the effluent raw gas would give off its heat.

This heat would then be transferred to the purge gas upon cycling. The same means could be utilized in a case where the purge gas to begin with is cooler than the raw gas.

The heat of adsorption, which becomes available from the adsorption of larger vapor or gas masses, which gives a higher temperature to the adsorbent which is to be loaded, can, in accordance with this invention, be also utilized in that cycling occurs when a certain temperature has been reached at a certain point, for example, in the center of the adsorbent just being loaded. In this manner, the temperature increase of the adsorbent also remains available to assist the following partial off-loading.

The temperature rise can be used in such manner that the adsorber will switch itself, through a suitable arrangement. This can, for example, be accomplished through a contact thermometer which would be built into the adsorber and which through relays would close a circuit which would accomplish the switchover.

The process can be explained further on an example: A r with 0.03 percent CO<sub>2</sub> at pressure of 1.4 ata. and normal temperature is leing passed through 2/parallel arranged adsorbers which are filled with charcoal of a length of 1.5 meters and a velocity of 600 cubic meters per cubic meters of adsorbent per hour. After ten minutes of on-loading time, the adsorber is being switched in known manner and following this the now loaded adsorber is being purged with CO<sub>2</sub> free nitrogen at 1.15 ata. at the same temperature and at a velocity of 2400 cbm per cbm adsorbent per hour. At the same time, the second adsorber which had been partially unloaded, while the first adsorber was previously being loaded, is now being loaded. The purity effect after 100 hours of cycling, is 99.5 percent corresponding to 0.00015 percent of CO<sub>2</sub> in the effluent gas.

The obtained advantages, as the example shows, lie in the high purifying effectiveness of the adsorbent which, in the foregoing example, was loaded only up to 20 percent of its equilibrium value, i.e., with 0.07 cubic meter CO<sub>2</sub> per gram of charcoal. This was accomplished by means of short cycling avoiding the adsorber becoming uneconomically big in size. When the raw gas contains a higher concentration of adsorbate, there is a special advantage in the short cycle time because practically the entire heat of adsorption remains in the adsorber and becomes available for the following desorption cycle. It is, therefore, possible to remove impurities in vapor form from gases also at lower pressure which otherwise would have been done at higher pressure (due to the relative lower vapor content) without imparing the purifying action and with little energy expenditure.

Patent Claims:

- (1) A process to separate adsorbable components from a gaseous mixture by means of periodically cyclable, through adsorbate-free purge gas partially regenerated adsorbents, characterized in that the adsorbent is loaded only to less than 50 percent of its equilibrium load and less than 90 percent of its breakthrough load value, in which one then switches to the second container, which has been partially regenerated in the meantime, while the first container is being partially unloaded with unneeded purge gas in the opposite direction, whereby the cycle time is between five and thirty minutes.
- (2) A process in accordance with Claim 1 characterized in that the partial loading takes place at ambient temperature as well as at the same temperature as the partial unloading and whereby a purge gas volume is passed through the adsorbent of three to four times the effective raw gas volume.
  - (3) A process in accordance with Claim 1 and 2 characterized in that one uses an adsorbent material of high selective capacity for the to be separated component.
  - (4) A process in accordance with Claims 1 through 3 characterized in that one uses adsorbent material with particle size between 1 and 2 mm.
  - (5) A process in accordance with Claim 1 through 4 characterized in that one uses an adsorbent material layer with a cross-section of from one-half to one qm per thousand characteristic flowing gas of at least a length of 1-1/2 meters.
  - (6) A process in accordance with Claims 1 through 5 characterized in that when one has the same standard volume of raw and purged gas, the raw gas pressure is a h 3 to 4 times higher than the purged gas pressure.
  - (7) A process in accordance with Claims 1 through 6 characterized in that when there is a lesser ratio between raw gas and purge gas than 1: 3 to 4, one uses a temperature of three degress higher purge gas for each halving of the ratio (lower limit).
  - (8) A process in accordance with Claims 1 through 7 characterized in that one can lower the temperature level of the adsorption and desorption in relation to the ambient temperature.

- (9) A process in accordance with Claims I through 5 characterized in that, in accordance with known practice in the interest of heat exchange between loading and unloading, process (at higher concentration of the separable components), one builds the adsorbed vessels into one another in the form of a heat exchanger to obtain thermic contact with each other.
- (10). A process in accordance with Claims 1 through 9 characterized in that one cycles the adsorbers automatically as soon as a certain temperature has been reached in the adsorbent caused by the adsorbing of larger gas and vapor quantities.

References: German Patent No. 624912

German Patent No. 704073; Bratzler; "Adsorption of Gases and Vapors," 1944, Pages 107, 108, and 121.

PLAINTIFF'S EXHIBIT 5E

British Patent Specification No. 677,150

#### PATENT SPECIFICATION 677,150



Date of Application and filing Complete Specification: Nov. 25, 1949. No. 30275/49.

Application made in Germany on Nov. 25, 1948.

Complete Specification Published: Aug. 13, 1952.

Index at acceptance:-Class 1(i), L1.

#### COMPLETE SPECIFICATION

#### Improvements in or Relating to the Purification of Gas Mixtures

We, GESELLSCHAFT FUR LINDE'S EISMASCH-INEN A.G., a corporation organized under the laws of Germany, of Hollriegelskreuth, B. Munchen, Germany, do hereby declare the 6 nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:-

This invention relates to gas purification 10 processes and is more particularly concerned with a process for the separation of impurities from gas mixtures by the removal

thereof by an adsorbent.

The removal of adsorbable constituents from gas mixtures by means of adsorbers adapted to be periodically changed over and capable of regeneration by means of washing gas free from adsorbate is at present practised. The adsorbent is charged up to about 20 50%-75% of its maximum capacity, which is known as the equilibrium charge. The value actually reached, which is known as the break-through charge, is attained when the concentration of the adsorbable con-25 stituent in the end product suddenly commences to rise rapidly from a small constant or slightly varying value.

Research is constantly being carried out to find conditions under which the capacity of 80 the adsorbent is increased. Vapours of the gas constituents, whose liquid phases also exist at room temperature, such as the vapours of water or organic solvents, are so readily adsorbed at room temperature by adsorption media such as gels, that break-through charges of between 55% and 80% of the equilibrium charge of 35% by weight, according to the length of the layers, that is, a total charge of about 20% by weight, are 40 obtained in the neighbourhood of their dew point. Benzene is adsorbed under similar conditions and to a similar order of magnitude by activated charcoal. Conditions are different when it is endeavoured to remove low-boiling gases, for example the carbon dioxide of the atmospheric air, by adsorption far below their dew-point concentration. Owing to the partial pressure of the carbon dioxide in the air, that is, c.2 mm. Hg., an

equilibrium charge of only about 0.32 cc. of 50 CO, per gramme of charcoal = 0.06% of the weight of charcoal, is obtained at normal temperature. If it is endeavoured to purify the air by adsorption through charcoal and to charge the charcoal in the usual way to 55 about one-half of this equilibrium value, satisfactory purification is nevertheless not obtained. Experiments have shown that removal of the carbon dioxide from the gas sufficient to produce a purifying effect of 60 about 99% is only achieved with a substantially lower charge, lying at about 0.07 cc. per gramme of adsorbent = 22% of the equilibrium charge. (When a lower purifying effect is required, higher charges can be permitted.) Because of this, there is no known method for the large scale removal of lowboiling gases from gas mixtures by the use of adsorbents, since intolerably high quantities of adsorbent would have to be used. A substantial shortening of the adsorption/ desorption periods (to save adsorbent) meets with the difficulty that in the desorption the heating and re-cooling of the adsorbent to the adsorption temperature, as hitherto 75 adopted, cannot be carried out in a sufficiently short time, especially as it is the adsorbate, which lies on the adsorbent in low concentration, which is difficult to remove.

However, it has been established that the 80 regeneration can be carried out in a short time, even with small charges, if certain conditions are observed. Thus, it is possible to remove practically completely even the smallest quantities of low-boiling gases, such 85 as CO,, from gas mixtures such as air, at normal pressure and normal temperature, with a constant high purifying effect of 99% if the adsorbent is charged from a residual charge up to only about 20%-25%, of its equilibrium charge with the gas to be separated. e.g. CO, and if the amount of the added charge is removed at the same temperature with an excess of washing gas.

Experiments have shown that 10 minutes are sufficient to remove the amount of the added charge of carbon dioxide, without any increase in temperature, with a quantity of

[Price 2/8]



washing gas equal to about 3-4 times the effective volume of untreated gas. By "effective volume" is meant the volume actually occupied by the gas, which varies substantially in inverse proportion to the pressure with the same weight of gas. The residual charge amounts, under these conditions, to about \$50 and the quantity added in each case to about 14%, of the equilibrium 10 value. It will hereinafter be called the additional charge. The same purifying effect can be continuously maintained and similar conditions exist for other gases having similar properties. For high purification it is im-15 Portant that the additional charging should not continue until the break-through of the component to be separated, but should be stopped, in the extreme, at 90% of the breakthrough charge. A sufficient layer of in-20 completely charged adsorbent is thus maintained, which produces a high purification.

According to the present invention there is provided a process for the separation of adsorbable constituents from gas mixtures by 25 me as of two adsorbers which are arranged to be periodically changed over and partially regenerated by we bing was free from adsorbate, wherein the gar mature is passed through the first adsorber until the adsorbent therein is charged to below 50% of its equilibrium charge and below 90% of its breakthrough charge, the gas mixture then being passed through the second adsorber whilst the first adsorber is partially regenerated with washing gas, the gas mixture being redirected through said first adsorber when said second adsorber has been charged in a similar manner to said first adsorber. The adsorption/desorption time is substantially
between 5 and 30 minutes. At approximately atmospheric pressure, the adsorption/ desorption time is in the neighbourhood of the lower limit, whilst at increased pressure it is in the neighbourhood of the upper limit, 45 since with increased pressure the capacity of the adsorbent also increases. Similarly, when high purification is desired, the adsorption/desorption time will be moved nearer to the lower limit. These short adsorption/ reduce the quantity of adsorbent to an eco-nomically tolerable value. However, the adsorption/desorption time cannot usually be reduced below the lower limit stated, 55 since part of the carrier gas for the impurities. which is generally produced in the pure state or worked up, is adsorbed at the same time and this part is displaced in the subsequent washing period by washing gas, ad-60 mixed to this and is therefore lost. If adsorption- or desorption-time is too small, the relative amount of such losses may be too great and may prevent an economic process.

The purifying effect is particularly high 65 when the adsorbate-free pure washing gas

flows through the adsorbent in countercurrent flow to the untreated gas in the partial discharge. In this case, the washing gas is so well utilised that a volume of washing gas equal to three to four times the volume of untreated gas is sufficient to dis-charge the adsorbate to such an extent that a purification of more than 99% is continuously ensured without the washing gas having to be heated above the temperature 75 of the untreated gas. The process can in principle be carried out with all types of adsorbent. However, it is expedient to employ adsorbents having particularly high adsorption capacity, and preferably those 80 which, owing to the selective adsorption of the impurities to be separated, have a particularly high capacity therefor, whilst the carrier gas is relatively less readily adsorbed. Similarly, it has been found that the grain 85 size of the adsorbent material has a great influence in the sense that the efficiency of the purification increases with the fineness of the grain structure. Theoretically, this is to be expected, but having regard to the danger 90 of adsorbent with very small grains being carried along and having regard to the pressure drop caused by the adsorbent, the grain size should not be excessively small but should be of the order of 1 to 2 mm. Within 95 this range tolerable pressure drops are incurred, especially if the cross-section of the layer of adsorbent amounts to between 0.5 and 1 sq. m. per 1000 cubic metres of gas flowing per hour. The layer of adsorbent 100 should, in view of the high purification desired, be at least 1.5 metres long. The upper. limit depends upon the permissible pressure drop and the amount of adsorbent, which is limited by reason of the simultaneous ad- 105 sorption of the carrier gas.

If the gas is under pressure, in which case the effective volume of the compressed gas is inversely proportional to the pressure, the volume ratio between the washing gas and the untreated gas, when using equal volumes of gas at normal pressure, is maintained at 3.4 to 1 if the pressure of the untreated gas is three to four times as high as the washing Thus, for example, if the normal volumes, measured at 1 atmosphere absolute pressure, of the untreated gas and the washing gas are equal and the washing gas pressure is equal to 1.1 atmospheres absolute pressure, an untreated gas pressure of 3.3 to 120 4.4 atmospheres absolute pressure is suffi-cient to conform to the above-stipulated ratio of 3-4/1. If the degree of purity is not sufficient, an improvement can be effected by increasing this ratio, or if this is not possible, 125 by shortening the adsorption/desorption time within the above limits, provided that the loss of carrier gas is still tolerable.

If the available quantity of washing gas is not sufficient, heating by a few degrees will 180

suffice to achieve the desired result with smaller quantities of washing gas. crease in the mean temperature level of the partial discharge by at least 3° C. relatively to the additional charging operation is suffi-cient to halve the ratio of the volume of washing gas to volume of untreated gas. The fact that the quantity of adsorbent must still be relatively large owing to its low charge is counter-balanced by this rational utilisation of the washing gas and by the fact that large quantities of energy are not employed for the pre-heating thereof. On the other hand, there is the advantage that owing to the larger cross-sections of the adsorbers employed the pressure loss of the flowing gas is smaller and the energy consumed to overcome the resistance to flow is smaller. The general temperature level in the charging and discharging can be higher or lower than the ambient temperature. By shortening or lengthening the adsorption/desorption times it will be possible to adapt the operation to varied conditions without any substantial alteration being necessary of the proportion of washing gas to the quantity of untreated gas. It is also possible, in order to be able to operate successfully with substantially smaller quantities of adsorbent, to work at a temperature level lower than the surrounding atmosphere, especially if the untreated gas must in any case be cooled for the purpose of further separation. If the concentration of the constituents to

85 be separated is high, the two adsorbers may be built one within the other in a manner known per sc in the same way as heat exchangers in order to dissipate the adsorption heat. The adsorption heat then assists the discharging operation and the desorption cold assists the charging operation.

A heat exchange can also be effected between the two adsorbents by providing in a manner known per se accumulator masses to 45 which the effluent treated gases yield their heat. This heat is in turn transmitted to the washing gas after the change-over. The same means can be employed if the washing gas is colder at the beginning than the untour treated gas.

The adsorption heat liberated in the adsorption of large quantities of vapour or gas, which imparts a higher temperature to the adsorbent being charged, may be utilised to effect the change-over between the two adsorbers when a predetermined temperature merease is reached at a temperature point, for example in the centre of the adsorbent being charged. In this way, the temperature increase of the adsorbent is also maintained so as to assist in the subsequent partial discharge. This can be effected, for example, by providing in the adsorbent a contact thermometer of a known type which closes, in the manner of a relay, a circuit

containing the change-over arrangement.

The process will be more fully explained with reference to an example: Air containing 0.03% carbon dioxide is passed at 1.4 atmosphere absolute pressure and at normal 70 temperature through one of two parallel-connected adsorbers filled with a layer of activated charcoal of length 1.5 m., at an hourly rate of 600 cb.m. per cb.m. of ad-After a charging period of 10 minutes, the adsorbers are changed over in known manner, and the charged adsorber is washed, for ten minutes, with nitrogen free from carbon dioxide at 1.15 atmospheres absolute pressure, at the same temperature 80 and at an hourly rate of 2400 cb.m. per cb.m. of adsorbent, while the partially discharged second adsorber which has meanwhile been washed, is charged. The purifying effect amounts after 100 hours alternate operation 85 to 99.5%, corresponding to 0.00015% of carbon dioxide in the end gas.

The advantages of the process will be seen from the example. The adsorbent has a high purifying action, owing to the short adsorption/desorption period, without the adsorbers having to be of uneconomically large dimensions. When the untreated gas contains higher percentages of adsorbable constituent, another advantage of the process is 95 that, owing to the short adsorption desorption time, practically the whole of the heat of the adsorption process remains in the adsorber and is consequently usefully employed for the subsequent desorption. possible to carry out the removal of vaporous impurities from gases, which are usually preferable effected at fairly high pressures (owing to the lower relative vapour content), at lower pressures without any loss in the purification factor and with a smaller consumption of energy

In Specification No. 633,137 it is stated that it is known to effect the separation of carbon monoxide and hydrogen, i.e. of gases the adsorption constants of which in relation to the adsorption medium, in this case active carbon, lie close together, by selective adsorption in streams of gaseous mixtures, by reversing in rapid succession, for example every three or six minutes, the charging and discharging of each unit of a cyclically operated adsorption medium and by interrupting the adsorption long before reaching adsorption equilibrium, whereupon the adsorption 120 medium, prior to, the next charging step, is caused to revert to the original condition of full adsorptivity by desorption in the same range of temperature (short phase process).

Specification No. 633,137 is concerned with an improvement in this known process by prolonging the duration of the individual desorption steps in relation to the duration of the adsorption steps.

Having now particularly described and 130

ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the separation of adsorb-5 able constituents from gas mixtures by means of two adsorbers which are arranged to be periodically changed over and partially regenerated by washing gas free from adsorbate, wherein the gas mixture is passed through the first adsorber until the adsorbent therein is charged to below 50% of its equilibrium charge and below 90% of its breakthrough charge, the gas mixture then being passed through the second absorber whilst 15 the first adsorber is partially regenerated with washing gas, the gas mixture being re-directed through said first adsorber when said second adsorber has been charged in a similar manner to said first adsorber, the adsorption/desorption time being substantially between 5 and 30 minutes.

Process as claimed in claim 1, wherein the partial charging and regenerating is carried out at the temperature of the surrounding atmosphere and a volume of washing gas equal to 3 to 4 times the effective volume (as herein defined) of untreated gas is passed through the adsorbent.

3. Process for the separation of adsorbable constituents as claimed in claims 1 or 2, wherein the washing gas flows in the opposite direction to that of the treated gas.

4. Process as claimed in any of the preceding claims, wherein adsorbents with a high selective capacity for the constituent to be separated are employed.

 Process as claimed in any of the preceding claims, wherein the grain size of the adsorbents employed is between 1 and 2 mm.

6. Process as claimed in any of claims 1 to 5, wherein the cross-sections of the adsorbent layers employed are from 0.5 to 1 square metre per 1,000 cubic metres of gas flowing through per hour, the length of the layers being at least 1.5 m.

7. Process as claimed in any of claims 1

to 6, wherein with the same volume of untreated gas and washing gas at normal pressure, the pressure of the untreated gas is made three to four times higher than the pressure of the washing gas.

8. Process as claimed in claim 1, wherein when the volume of washing gas is less than three to four times the effective volume (as herein defined) of untreated gas, a higher temperature of at least 3° C, is employed for the washing gas for each halving of the ratio of the volume of washing gas/volume of untreated gas

9. Process as claimed in any of claims 1 to 8, wherein to facilitate a heat exchange between the charging and discharging adsorbents (at higher concentrations of the constituents to be separated) the two adsorbers are built one within the other in a manner known per se in the same way as heat exchangers and are thus brought into thermal contact with one another.

10. Process as claimed in claim 1, wherein the temperature of adsorption and desorption is lowered with respect to the surrounding atmosphere.

11. Process as claimed in any of claims 1 to 10, wherein the adsorbers are automatically changed over as soon as a predetermined temperature increase, due to the quantities of gas and vapour adsorbed, is reached at a measuring point in the adsorber being

12. Process for the separation of adsorbable constituents from gas mixtures substantially as described hereinbefore.

Dated this 25th day of November, 1949.

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### PLAINTIFF'S EXHIBIT 5F

Kahle, H. "Die 'reversible' Adsorption als Mittel zur Vorreinigung und Zerlegung von Gasgemischen," Chemie-Ing.-Techn. 25 Jahrg. 1953/Nr. 3, pp. 144-48 and translation.



# Die "reversible" Adsorption als Mittel zur Verreinigung und Zerlegung von Gasgemischen

Von Dr.-Ing. HEINRICH KAHLE, Gesellschaft für Linde's Eismaschinen AG., Höllriegelskreuth

An Hand von Diagrammen und schematischen Ausführungsbeispielen werden Grundlagen sowie apparative und verfahrensmäßige Voraussetzungen für eine annähernd reversible Gasreinigung und Trennung durch Adsorption zwecks extremer Reinigung des behandelten Gases erläutert. Die Voraussetzungen sind: Kombination von Adsorbern mit Wärmeaustauschern an beiden Enden des Adsorbers, Be- und Entladungsbegrenzung des Adsorbers sowie Gegenstromentladung mit adsorbatfreien Spülgasen.

Streng reversible Prozesse sind in der Technik weder bekannt, noch erscheinen sie realisierbar. Es gibt aber einige Verfahren, insbesondere in der Gaszerlegungstechnik bei tiefen Temperaturen, die sich einer "reversiblen" Arbeitsweise nahern. Dabei sei als "reversibel" eine Arbeitsweise bezeichnet, die einen technisch derzeit möglichen maximalen Wirkungsgrad besitzt oder sich ihm nähert. (Dieser ist seinerseits wiederum ein Teil dessen, was bei theoretisch reversiblen Arbeitsvorgängen erreicht werden könnte.) Der Vorgang der Erwärmung und Wiederabkühlung eines Gases kann als nahezu "reversibel" bezeichnet werden, wenn er mit Hilfe eines Gegenstromwärmeaustauschers mit möglichst geringer Temperaturdifferenz durchgeführt wird.

Auch für den Stoffaustausch sind derartige Arbeitsweisen bekannt geworden. Z. B. stellt die Rektifikation eine der Reversibilität sich nähernde Arbeitsweise bei der Stofftrennung dar. In dieser Hinsicht bemerkenswersind auch Verfahren, bei denen die Lösungswärme des Waschvorganges für die Zwecke der mit Wämzaufnahme einhergehenden Entgasung des beladenen Waschmittels bei geringer mittlerer Temperaturdifferenz zwischen beiden Vorgängen nutzbar verwendet wird. Oft werden dabel erhebliche Temperaturbereiche durchlausen, z. B. wenn die Lösungsvorgänge bei tiesem Temperaturniveau vor sich gehen. Die beiden Vorgänge des Energie- und Stoffaustausches gehen hierbei parallel.

#### Energie- und Stoffaustausch in Regeneratoren

Energie- und Stoffaustausch kann auch in Regeneratoren bei richtiger Bemessung derselben und der Umschaltzeiten selbst über große Temperaturdifferenzen hinweg weitgehend reversibel durchgeführt werden, besonders wenn die auzutauschenden Stoffmengen in mäßiger Konzentration vorliegen.

Es sei das Beispiel des Kälteaustausches mit gleichzeitigem Stoffaustausch zwischen Rohgas und Spülgas in Kälteregeneratoren erwähnt.

Bild 1 zeigt eine übliche Regeneratorenanordnung in einem Zerlegungsapparat mit zwei gleichen, periodisch und regelmäßig umgeschalteten, mit Speichermasse gefüllten Regeneratorenästen nebst den zugehörigen Schaltorganen, deren Wirkungsweise schematisch dargestellt ist. Der Betriebszustand vor Umschaltung ist durch ausgezogene Pfeile, der Betriebszustand nach der Umschaltung durch gestrichelte Pfeile angedeutet. Der am oberen und unteren, schematisch dargestellten Umschaltorgan eingezeichnete Diagonalbalken verbindet nach jeder Drehung um 90° die Eintrites- bzw. Austrittsleitungen für zu- und abströmendes Cas, jeweils mit dem anderen Ast der Einrichtung. Das Rohgas mit den kondensierbaren Verunreinigungen tri't bei der dargestellten Schaltung durch den linken Regenerator mit etwa 25 °C ein, gibt seine kondensierbaren Anteile durch Kondensation an die in der Periode vorher kallgeblasene Speichermasse ab und tritt als gereinigtes Gas mit tiefer Temperatur (z. B. -150 °C) über die obere Umschaltvorrichtung aus,

um zum Zerlegungsapparat geführt zu werden. Gleichzeitig strömt reines Spülgas, z. B. ein Zerlegungsprodukt durch die obere Umschaltung in den rechten Speicher mit —155° ein und bei der unteren Umschaltung, beladen mit den Verunreinigungen, die es durch Verdunsten aufgenommen hat, mit etwa 20° aus.

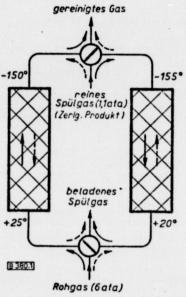


Bild 1. Schematische Darstellung des Regeneratorbetriebes

→ Betriebszustand vor Umschalten, → → Betriebszustand

pach Umschalten

Der Temperaturverlauf für ein Gasteilchen längs der Speichermasse im Regenerator, wie er sich im Beharrungszustand am Ende der Rohgasperiode bzw. am Ende der Spülgasperiode also kurz vor der Umschaltung einstellt. ist durch das Diagramm, Bild 2, im Prinzip dargestellt. Das kurz vor der Umschaltung auf die Schicht gelangende Gas ändert, wie ersichtlich, auf der Anfangsschicht der Speichermasse seine Temperatur zunächst nur wenig, da sich diese Schicht während der vorhergehenden Strömung des mit konstanter Temperatur eintretenden Gases bereits an dessen Temperatur angeglichen hat. Erst im weiteren Verlauf der Schicht fällt die Temperatur des Rohgases ab, bzw. steigt die des Spülgases an. Zu allen anderen Zeitpunkten, die zwischen zwei Umschaltungen liegen, verlaufen die Temperaturlinien der strömenden Gase zwischen der dick gestrichelten und der ausgezogenen Kurve, wobei jeweils senkrecht untereinanderliegende Punkte auf diesen beiden Kurven die beiden Temperaturextreme in jedem Querschnitt der Speichermasse darstellen. Die Temperatur der Speichermasse selbst bewegt sich ebenfalls zwischen jenen zwei Kurven. Ihr Temperaturmittel ist im Beharrungszustand konstant und entspricht etwa der strichpunktierten Kurve. Eines der Kennzeichen des Regeneratorbetriebes ist dieses konstante Temperaturgefalle in der Speichermasse, das von Art und Menge der Masse sowie Temperaturzustand und Zusammensetzung des Rohgases und des Spulgases abhängig ist.

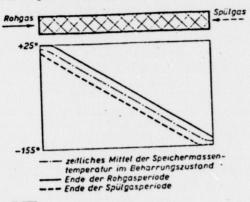


Bild 2. Der Temperaturverlauf im Re erator

Enthält das Rohgas kondensierbare Bestandteile, so wird zu einem bestimmten Zeitpunkt, der vom jeweils herrschenden Betriebszustand abhängig ist, und in einem bestimmten Bereich der Speichermasse Kondensat aus dem Rohgas einerseits abgeschieden und in das Spülgas andererseits in einer im voraus zu berechnenden Menge verdunstet; denn jeder Temperatur ist ein bestimmter Sättigungsdruck des kondensierten Anteils zugeordnet. In bestimmten Temperaturdisserentialen im Sättigungsgebiet wird stets ein bestimmter Betrag an Kondensat in dem "warm zu blasenden" Regenerator abgeschieden, bzw. in dem anderen "kalt zu blasenden" Regenerator verdunstet. Gleichzeitig wird einerseits ein bestimmter Betrag an Kondensationswärme frei bzw. andererseits gebunden. Diese positive bzw. negative Wärmetönung überlagert sich dem normalen Energieaustausch zwischen dem latenten Wärmeinhalt des Spulgasstromes einerseits und des Rohgasstromes andererseits über die Speichermasse als Zwischenträger, die sowohl die positive als auch die negative Wärmetönung zunächst speichert, um sie nach der Umschaltung an die andere Gasart abzugeben. Der Vorteil dieser Art des Energie- und Stoffaustausches gegenüber den üblichen Reinigungs- und Zerlegungsverfahren, bei denen die Kondensation aus einem mehrkomponentigen Gasgemisch oft in einem tieferen Temperaturniveau vorgenommen werden muß als die Verdampfung, besteht darin, daß eine Verdunstung der Kondensate im Strom des Spülgases und der Zerlegungsprodukte in annähernd dem gleichen oder einem noch tieferen Temperaturniveau eintritt als die Kondensation. wodurch eine angenähert reversible Arbeitsweise erreicht

Die bei der Kondensation frei werdende Wärme wird von den Speichermassen zwar im wesentlichen aufgenommen, Reste gehen jedoch mit dem Rohgasstrom in Zonen tieferer Temperatur. Auch die bei der Verdunstung frei werdende Kälte wird teilweise in Zonen höherer Temperatur getragen und trägt zur Vergrößerung der im Interesse des guten Wärmeaustausches möglichst klein zu haltenden Temperaturdifferenzen an den Wärmeaustauscher-Enden in unerwünschter Weise bei, vor allem wenn erheblichere Mengen von Kondensat augeschieden und wieder verdunstet werden.

### Energie- und Stoffaustausch in mit Regeneratoren kombinierten Adsorbern

Dem vorbeschriebenen Verfahren der Gasbehandlung in Regeneratoren sei ein solches in Adsorbern gegenübergestellt, wobei die Adsorber in bestimmter Weise mit Regeneratoren kombiniert und betrieben werden. Diese

Verfahren, welche eine interessante Parallele zu dem vorbeschriebenen Vertahren bilden, seien als Sorbogen-Verfahren bezeichnet. Eine Kombination ist in Bild 3 dargestellt<sup>9</sup>).

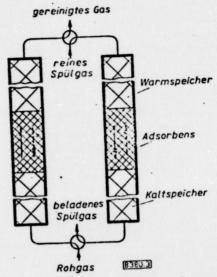


Bild 3. Schematische Darstellung des mit Regeneratoren arbeitenden Sorbogen I-Verfahrens

#### Sorbogen I - Verfahren

In der kombinierten zweiästigen Einrichtung, die mit Rohgas bzw. Spülgas von etwa gleicher Temperatur beschickt wird, und die sich für jeden Ast aus einem Kaltspeicher, dem Adsorber und dem Warmspeicher zusammensetzt, stellt sich ohne äußeres Zutun, lediglich unter dem Einfluß der positiven Wärmetönung des Adsorptionsvorganges und der negativen Wärmetönung des Desorptionsvorganges, das Temperaturgefälle im Adsorber derart ein, daß die Temperatur von der Eintrittsstelle des Rohgases zum Reingasaustritt ansteigt. Es ergibt sich hierbei ganz von selbst, daß der Speicher auf der Rohgasseite die Funktion eines Kaltspeichers, der Speicher auf der Reingasseite die Funktion eines Warmspeichers übernimmt.

An den freien Enden der Speicher herrschen nach Bild 4 je nach dem jeweiligen Betriebszustand der Einrichtung von der Umgebungstemperatur nur wenig verschiedene, in geringen Grenzen schwankende Temperaturen. Die Temperatur eines mit Umgebungstemperatur in den Kaltspeicher einströmenden Rohgasteilchens sinkt also zunächst im Kaltspeicher, steigt im Adsorbens wieder bis auf über Umgebungstemperatur an, um längs der Schicht des Warmspeichers wieder auf etwa Umgebungstemperatur abzusinken.

In Bild 4 ist der Temperaturverlauf der Gase in den beiden Asten jeweils kurz vor der Umschaltung dargestellt. Im Interesse der vereinfachten Darstellung wurde hier und in Bild 8 das Stück des konstanten Temperaturverlaufes fortgelassen (vgl. Bild 2).

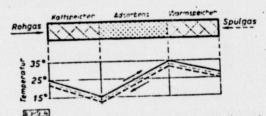


Bild 4. Temperaturverlauf im Kaltspeicher, Adsorber und Warmspeicher beim Sorbogen 1-Verfahren

röhmen wird dahur gesorgt, dan der Temperaturgradient sowohl im Adsorbens als auch in den Speichern autrecht erhalten bleibt. Das Spulgasteilchen, welches den jeweils beladenen Adsorber nach der Umschaftung einfladt, untgeliegt, wie ersichtlien, inmickeint wie das Kongas, da es entgegengeseizt zu diesem stromt, zunächst einem Temperaturanstieg über dem Warmspeicher, anschließend einem Temperaturabfall entlang der Adsorbensschicht, um anschließend über dem Kaltspeicher am anderen Ende des Adsorbens wieder auf Umgebungstemperatur angewärmt zu werden.

Die bei der Bindung adsorbierbarer bestandteile am \*Adsorbens freiwerdende Adsorptionswärme wird mit dem gereinigten Gas eine bestimmte Strecke in der Richtung der Strömung des Rohgases fortgetragen. Ein Teil der Wärme verbleibt auf dem Adsorbens selbst, da auch dieses ein gewisses Wärmespeichervermögen besitzt; der restliche Teil wird von der Speichermasse aufgenommen.

Umgekehrt werden bei der Entladung des Adsorbens entsprechende Kältebeträge frei bzw. Wärmebeträge gebunden, die teils aus der Adsorbensmasse selbst, teils aus dem Gas entnommen werden. Dabei kann die Temperatur wesentlich unter Umgebungstemperatur sinken. Die bei der Entladung erzeugte Kätte verbleibt nicht allein auf dem Adsorbens, sondern wird durch das Spülgas zum Teil auf den Kaltspeicher überträgen, in dem das mit Desorbat beladene Spülgas wieder auf etwa Umgebungstemperatur angewärmt wird.

Je größer die adsorbierten Beträge sind, um so größer ist nicht nur die Wärmeentwicklung bei der Adsorption, sondern auch die Kälteerzeugung bei der Desorption. Die Speichermassen an den Enden der Adsorptionsschicht sorgen dafür, daß die Wärmetönung des Adsorptionsvorganges, die sonst z. B. durch Kühlwasser abgeführt und vernichtet werden mußte, nunmehr nutzbringend für den gegenläufigen Desorptionsvorgang, der bisher durch Heizung unterstützt wurde, zur Verfügung steht.

Ersetzt man die Speicher an den Adsorbens-Enden durch Röhren-Wärmeaustauscher, so wird die gleiche Wirkung erreicht. Die Umschaltorgane liegen in diesem Fall zwischen den kontinuierlich betriebenen Austauschern und den Adsorbern, Bild 5.

Die bereits früher vorgeschlagene Anordnung des Adsorbens in den Rohren des Wärmeaustauschers und die Durchführung von Adsorption und Desorption in diesen dürfte die Wirksamkeit der obigen Anordnungen nicht ganz erreichen.

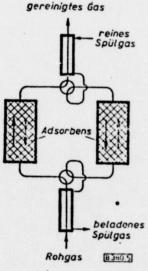


Bild 5 (links). Schematische Darstellung des mit Röhrenwärmeaustauschern arbeitenden Sorbogen I-Verfahrens

Daß dieser Vorgang der Beladung und Lutladung des Adsorbens auch bezugich des Spulgasverbrauchs angenahert reversibel vor sich geht und gleichzeitig hohe Reinigungsetiekte erzielt werden, kann durch zwei Arbeitsprinzipien bei der Beladung bzw. Entladung des Adsorbens erreicht werden. Sie seien hier als die Prinzipien der Teilbeladung und Teilentladung bezeichnete).

Daß im einströmenden Rohtjas das Adsorbens nicht bis zur Sattigung sondern nur bis zum sogenannten Durchbruchswert (d. h. dem Beladungswert des Adsorbens, bei dem die zu entferneede Komponente des strömenden Gases im austretenden gereinigten Gas erscheint) beladen wird, ist bereits seit langem allgemein bekannt. Will man jedoch hohe Reinheitswerte erreichen, so ist die Beladung des Adsorbens bis in die Nähe des Durchbruchswertes noch zu hoch.

Nach dem neuen Prinzip der Teilbeladung wird das Adsorbens nur bis zu einem Bruchteil des Durchbruchswertes beladen und die Beladung dann abgebrochen. Auf diese Weise bleibt eine relativ große Adsorbensschicht völlig unbeladen, was hingenommen werden kann, da die Eigenart des geschilderten Verfahrens und der Anordnung eine häufigere Umschaltung gestattet.

Durch Anwendung dieses Prinzips wurden in einer technischen Anlage, wie später beschrieben, erstaunlich hohe Reinigungsettekte bei Luft auch von verhältnismäßig schlecht adsorbierbaren Verunreinigungen wie CO; bei einer Temperatur erreicht, die man bisher als ungeeignet für diesen Zweck angesehen hat, zumal, wenn gleichzeitig von einer Erhitzung des Spulgases völlig abgesehen wird und das noch zu beschreibende Arbeitsprinzip der Teilentladung angewendet werden soll. Voraussetzung für den höchsten Reinigungseffekt ist selbstverständlich, daß das Spulgas von den zu entfernenden Bestandteilen völlig frei ist und stets in derselben, zur Rohgasströmung entgegengesetzten Richtung über das Adsorbens strömt. Das Prinzip der Teilentladung gründet sich auf die Überlegung, daß eine vollständige Entladung des Adsorbens einen zu hohen Spülgasaufwand erfordert, um es für die nachfolgende Periode der Beladung möglichst aufnahmebegierig zu machen.

Die beiden Arbeitsprinzipien seien durch Bild 6 erläutert, das sich auf Messungen gründet, die vor einiger Zeit im Laboratorium der Gesellschaft für Linde's Eismaschinen ausgeführt wurden, und über die später berichtet werden soil. Dabei wurde gefunden, daß man die bei Umgebungstemperatur (etwa 20°) über eine 1.5 m lange Schicht einer sog. Carbotoxkohle von 1 bis 2 mm Körnung geführte Luft von ihren Verunreinigungen u. a. auch von der schwer adsorbierbaren Kohlensäure mit einem Reinigungseffekt von erheblich über 99% entfernen konnte, wenn man, ausgehend von einer CO .-Restbeladung von etwa 8% des Sättigungswertes, die Kohle bis zu einem Wert von etwa 25% des Sättigungswertes belud und dann anschließend bei etwa gleicher Temperatur mit etwa der dreifachen Menge Spülgas im Gegenstrom bis auf den Restwert von etwa 8% wieder teilentlud.

In Bild 6 ist auf der Abszisse die Schichtlänge in Bruchteilen der Gesamtschichtlänge, auf der Ordinate die relative "Beladungshöhe" im vertikalen Querschnitt der

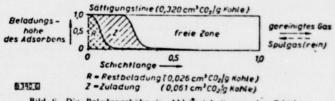


Bild 6. Die Beladungshöhe in Abhängigkeit von der Schichtlange bei Teilbeladung des Adsorbens

Schicht (des Adsorbens ist liegend gedacht) in Bruchteilen der maximalen (Seitigungs) Beladung aufgetragen. Die beiden Ssformagen Linien sind die Beladungstronten, welche die Sof. Zuladungszeite zu genicht schraftierti einschließen. Die linie Front begrenzt die Zone der dauernden Beladung bzw. Keistladung int doppelt schraffeit), die rechte Front die Zone der Zuladung im Ausgeblick der Umschaltung auf Gegenstromentladung. Zwischen dieser rechten Sstormigen Beleiningstront und dem Schichtende liegt die unbeladene Zone. Über diese und ähnliche Messungen wird in einer spateren Arbeit berichtet werden.

Dadurch, daß im Gegenstrom zum Rohgas über das zu entladende Adsorbens stromendes Spülgas zum Schlusse die ständig im Sättigungszustand befindliche Adsorbensschicht bespalt, kann sich das Spulgas bis zum Schluß der Spulgasperiode mit einem Maximum an desorbierten Bestandteilen aufladen. Die Spülung wird beendet, wenn die Aufladung des Spülgases wesentlich absinkt. Man kann bei isothermer Teilbeladung und Entladung bei gleichem Gesamtdruck mit etwa dem drei-·fachen Spülgesvolumen rechnen, wenn man gleichzeitig höchsten Reinigungseffekt verlangt. Mit zweifacher Spülgasmenge sinkt der Reinigungseffekt etwas ab. Bei je 5°C höherer Spülgastemperatur erniedrigt sich das Verhältnis des Spülgas- zum Rohgasvolumen jeweils auf die Hälfte, so daß man bei einer um 10° höheren Temperatur bereits weniger Spülgas als Rohgas benötigt3).

Es ist Sache der Planung, die Forderung, das vorhandene Spülgas gut auszunützen, mit der Forderung nach gutem Wärmeaustausch in Einklang zu bringen. Es ist jederzeit möglich, die angegebenen Richtwerte um Bruchteile zu überschreiten, so daß beiden Forderungen, die sich nicht widersprechen, leicht gerecht zu werden ist.

Der Umstand, daß man bei isothermer Entladung ein Mehrfaches des Rohgasvolumens an Spülges benötigt, zeigt, daß man trotz dieser sparsamen Arbeitsweise doch mit einer gewissen Hysterese rechnen muß. Abgesehen davon, daß man völlige Gleichgewichtseinstellung zwischen adsorbierter Phase und Gasphase nicht erwarten kann, hängt der Mehrverbrauch an Spülgas mit der Temperatursenkung zusammen, die sich bei der Entladung des Adsorbens in der zuletzt gespülten noch verhältnismäßig hoch beladenen Adsorbensschicht einstellt. Im Labormaßstab, d. h. bei großer Oberfläche im Verhältnis zur Masse und guter Wärmeab- bzw. Zustrahlung ist die-

Spülgas Warmspeicher

Heizung Adsorbens

Kühlung W

Kaltspeicher

Bild 7. Schematische Darstellung des Sorbogen II-Verfahrens

ser Effekt kaum merklich, bei einer technischen Anlage konnte er jedoch deutlich beobachtet werden, Die Anordnung der Speichermassen an den Enden der Amorbensschicht bedingt es, daß sich dieser Effekt nicht ungunstiger auswirkt. Als Folge der Anwendung des Teilentladungsprinzips läßt die im Adsorbens noch vorhandene Restbeladung langs der Restbeladungstront die Adsorptionswarme während der Beladung nicht auf einem räumlich engen Bereich, sondern auf eine größere Strecke verteilt frei werden, wodurch der bereits oben erwähnte Temperaturanstieg gegen das Adsorbens-Ende hin und ein besserer thermischer Wirkungsgrad erzielt wird. In einem völlig entladenen Adsorbens würden dagegen auf kleinem Raum große Wärmemengen frei werden, was vom Standpunkt des reversiblen Arbeitens gesehen besonders dann ungünstig ist, wenn wie bei dem Sorbogen II-Verfahren, Bild 74, aus besonderen Gründen der Temperaturgradient längs der Adsorbensschicht durch Heizbzw. Kühleinrichtungen zwischen Austauschern und Adsorbern vergrößert wird, um etwa fluchtigere Verunreinigungen bzw. Gasbestandteile zu binden und evtl. anzureichern.

#### Sorbogen II - Verfahren

Hierbei werden eine Kühleinrichtung am Rohgaseintrittsende, z. B. zwischen Kaltspeicher und Adsorbens, bzw. eine Heizeinrichtung am Reingasaustrittsende, z.B. zwischen Warmspeicher und Adsorbens, angeordnet. Diese Einrichtungen erlauben, Heizung und Kühlung in beiden Asten gleichzeitig und ständig zu betreiben. Dadurch wird Zeit gewonnen für das Vorkühlen bzw. Vorerhitzen der Speichermassen, die das Rohgas vorkühlen bzw. das Spülgas vorerhitzen sollen. Die gegenseitige-Beeinflussung von Heiz- und Kühleinrichtung wird durch die regelmäßige Umschaltung und die ständige Aufrechterhaltung eines Temperaturgefälles längs der Adsorbensschicht verhindert. Je nach dem Strömungszustand in der gerade herrschenden Schaltperiode kühlt die Kühleinrichtung entweder das Rohgas vor seinem Eintritt in das Adsorbens oder nach Umschaltung das austretende beladene Spülgas vor dessen Eintritt in den Kaltspeicher, der nun nach vorübergehender Teilanwärmung durch Rohgas wieder teilweise kaltgeblasen wird, Bild 7. Die Heizeinrichtung erhitzt in einer Periode das über dem Warmspeicher vorgewärmte Spülgas, bevor es auf das Adsorbens trifft. In der darauf folgenden Periode erhitzt sie das gereinigte Gas, bevor es auf den anschließenden, vorher teilgekühlten Warmspeicher trifft. Der Warmspeicher kann daher nach der Umschaltung zuströmendes Spülgas wirksam vorwärmen. Selbstverständlich liegen auch bei dieser Anordnung Adsorbens und Speichermassen im dauernd aufrecht erhaltenen Temperaturgefälle, wobei das freie Ende der Speicher sich stets annähernd auf Umgebungstemperatur befindet, Bild 8. Auch hier ist

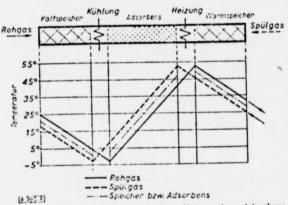


Bild 8. Der Temperaturverlauf im Kaltspeither, Adsorbens und Warmspeither beim Sorbogen II-Verfahren

· wiederum die Anderung der Temperatur eines durch die inrichtung strömenden Rongas- bzw. Spulgisteilchens kurz vor der Umschaltung schematisch dargestellt. Unter eem Linfluß von Heizung und Kuhlung überschneiden sich die Temperaturlinien von Roh- und Spülgas. Durch die strichpunktierte Linie ist wieder der Verlauf der Mitteltemperatur des Adsorbens bzw. der Speichermasse dargestellt. Günstig ist bei dieser Anordnung die Verstärkung des Heizungseffektes durch die gegen das Adsorbens-Ende getragene Adsorptionswärme und die Verstärkung des Effektes der Kühleinrichtung durch die gegen den Adsorbens-Anfang getragene Desorptionskälte. Auch diese Anordnung läßt eine angenähert reversible Arbeitsweise bis in Gebiete weit gesenkter Temperatur bei entsprechend großem Temperaturgefälle zu. Wie bereits oben erwähnt, ist ein Überschuß des Spülgasvolumens über das Rohgasvolumen bereits bei 10°C Temperaturerhöhung des Spülgases nicht mehr erforderlich.

Will man die adsorbierten Gasbestandteile wieder gewinnen, so genügt eine weitere Erhöhung der Temperaturdifferenz mit gleichzeitiger Verminderung der Spülgasmenge. Eine weitere Möglichkeit der Anreicherung besteht in der Desorption bei Unterdruck zweckmäßig und im Sinne der obigen Ausführungen unter Beibehaltung der Gegenstromspülung. Als Spülgas kann unter diesen Umständen auch ein vom gereinigten Gas hinter dem Adsorbens abgezweigter Teilstrom verwendet werden. Die Anwendung eines mäßig, z.B. auf 2 bis 10 atü erhöhten Druckes bei der Beladung des Adsorbens ist günstig, falls das gereinigte Gas unter Druck zur Verfügung stehen soll. Bei höheren Drucken steigen die Gasverluste beim Umschalten u. U. über einen zulässigen Wert, da auch ein Teil des gereinigten Gases adsorbiert wird und bei der Druckentlastung beim Umschalten verlorengeht. Über die technische Anwendung des Sorbogen I-Verfahrens sowie die vorbereitenden Versuche dazu soll in einer anschließenden, späteren Arbeit berichtet werden.

#### Zusammenfassung

Die verfahrensmäßigen und apparativen Voraussetzungen für eine angenaheit reversible Arbeitsweise (als Sorbogen I-Verfahren bezeichnet) bei der Reinigung von Gasen durch Adsorption bei verhältnismäßig kurzfristigem Wechsel der Adsorber vorzugsweise für die Zwecke einer weiteren Zerlegung des reinen Gases unter erhöhtem Druck und bei erniedrigter Temperatur werden erläutert. Das Verfahren wird infolge der Ahnlichkeit des Umschaltbetriebes sowie thermischer und stoffaustauschmäßiger Eigentumlichkeiten mit dem Verfahren der Gasreinigung durch Kälteregeneratoren verglichen.

An Hand von Schemazeichnungen und Diagrammen werden die Prinzipien des "reversiblen" Arbeitens, nämlich Wärmeaustausch zwischen Adsorptions- (Belade-) und Desorptions- (Entlade-)vorgang auch ohne Anwendung von fremden Heiz- und Kühlquellen erläutert. Eine Bedingung, um einen höchsten Reinigungseffekt auch bei der Entfernung schwer adsorbierbarer Verunreinigungen zu erreichen, ist die Aufrechterhaltung einer sehr großen freien (unbeladenen) Zone; dies wird als das Prinzip der "Teilbeladung" bezeichnet. Eine "reversible" Arbeitsweise wird durch Anwendung des Prinzips der "Teilentladung" gefördert. Die bekannte und folgerichtig stets angewandte Spülentgasung mit reinem Spülgas im Gegenstrom zum Rohgas ist eine weitere Voraussetzung sowohl für höchsten Reinigungseffekt als auch "reversibles" Arbeiten. Die Arbeitsweise für eine Anreicherung und Gewinnung adsorbierbarer Bestandteile (als Sorbogen II-Verfahren bezeichnet) unter Anwendung der gleichen Prinzipien und unter sparsamster Verwendung von Energie für Heizung und Kühlung nebst den apparativen Voraussetzungen hierfür wird angegeben.

Eingeg. 11. Aug. 1952 [B 380]

- 1) Dtsch. Patentanm. G 6724 IV b/12e.
- ) Dtsch. Patentanm. p 22 720 IV b/12eD.
- 3) Disch. Patentanm. G 405 IV b/12e.

#### 4) Disch. Patentanm. G 94 IV b/12e.

# BERICHTE AUS DER CHEMISCHER TECHNIK

### Versammlungsberichte

## Vortragstagung "Hochtemperaturtechnik" am 10. Oktober 1952 in Essen

Der Arbeitsausschuß "Hochtemperaturtechnik" im Fachausschuß Verfahrenstechnik des VDI trat am 10. Oktober 1952 zum ersten Mal mit einer Vortragstagung an die Offentlichkeit, nachdem er bisher über seine Arbeitssitzungen nur Kurzberichte veröffentlicht hatte¹)²). Sie fand gemeinsam mit dem Haus der Technik e. V., Essen, statt. Prof. Dr.-Ing. habil. K. Krekeler begrüßte die Versammlung, vor allem die ausländischen Gäste. Dir. Dr.-Ing. E. h. K. Rieß legte als Obmann des Fachausschusses die Gründe dar, die vor einigen Jahren zur Schaffung des Arbeitsausschusses geführt hetten, obwohl schon der Industrieofen-Ausschuß beim Verein deutscher Maschinenbau-Anstalten und verschiedene einschlägige Ausschüsse beim Verein deutscher Eisenhüttenleute bestenden. Er befaßt sich mit Problemen auf folgenden Gebieten:

- Physikalisch technische Grundlagen (Warmeübergang, Strömungsfragen, Fragen der Oberflächenreaktionen u. a.),
- Verbrennungs-, Vergasungs- und Entgasungstechnik (Gaserzeugung, Gas-, Kohlenstaub- und Olbrenner, Carburierung).
- 3. Ofenbau (konstruktiv, mit Wärmerückgewinnung),
- 4. Baustoff-Fragen,

 Meß- und Regeltechnik, deren Entwicklung selbst jedoch in den Händen des Normenausschusses für Meß- und Regeltechnik liegt.

In enger Beziehung zu den interessierten Kreisen der Praxis soll der Ausschuß die dringlichsten Aufgaben herausstellen, sie an die richtigen Stellen zur Bearbeitung leiten und sie finanzieren helfen. Wertvolle Hilfe wird hierbei das neue Institut für Verfahrenstechnik in Aachen leisten können.

Zum Abschluß teilte Dr. Rieß -- mit Worten des Dankes für die geleistete Arbeit -- mit, daß Prof. Joh. Körting aus Gesundheitsrücksichten sein Amt §ls Obmann niedergelegt und Dr.-Ing. A. Schuck es übernommen habe; dann übergab er die Leitung der Tagung an Prof. Dr.-Ing. F. Schuster.

Prof. Dr.-Ing. E. SCHWARZ VON BERGKAMPF, Leoben: Rationelle Modellhetrachtungen von Industrie-Ofen<sup>3</sup>)

Die Untersuchungen haben zum Ziel, an Hand von dimensionslosen Kenngrößen, wie der Revnolds-, Grashel- und Nußellschen Zahl, die Übertragung von Modellarößen auf große Betriebsausführungen von Ofen zu ermöglichen. Die Ergebnisse der durchgeführten Rechnungen stimmten überraschend auf überein mit einer großen Zahl von Ausführungen der verschiedensten Üben, wie Schachtofen (Hochölen, Kupolofen, Kalkofen usw.), Herdöfen nit flüssigem und festem Gut sowie Diebof. Die vom Redner eingelührten Vergrößerungsexponenten geben dem Ölenbauer wertvollen Auhalt bei seinen Berechnungen.

## THE "REVERSIBLE" ADSORPTION AS A MEANS FOR PRECLEANING

## AND FRACTIORATING OF GASEOUS MIXTURES

by Dr. -Ing. Heinrich Kahle, Gessellschaft für Linde's Eismachinen AG., Hollriegelskreuth

On hand of diagrams and schematic layout examples, the principles as well as the equipment and process foundations for an approximate reversible gas cleaning and separation through adsorption for the purpose of extreme purification of the process gas are explained. The requisits are: combination of adsorbers with heat exchangers at both ends of the adsorbers, loading and unloading limitation of the adsorbers as well as counter flow unloading with adsorbate-free purge gases.

Strictly reversible processes are neither known in the technique nor do they appear attainable. But there are some processes, particularly in the fractionating technique of gases at low temperatures which come close to a reversible operation. In this respect, a reversible operation shall be defined as one that has a technical maximum difficiency or approaches it. (This in turn is a part of what could be obtained in theoritical reversible work operations.) The operation of heating and re-cooling of gases can be called nearly "reversible" if it is done with the help of the counter flow heat exchanger with lowest possible temperature differential.

Also in the exchange of matter have such operating methods become known. For example, fractionating is an operating method that is approaching reversibility in the separation of matter. In this respect, worth noting are also processes where the heat of solution of the washing operation is used for the heat intake needed in the degasing of the loaded washing means at a small mean temperature differential between the two processes. Often considerable temperature spans are covered, i.e. when the solution processes are taking place at low temperature levels. The two operations of the energy and matter exchange are running parallel in this case.

# Paerey and Motter Eachdage in Regenerators

Energy and matter exchange can be reversibly accomplished to a large degree even over great temperature differentials with proper sizing and time cycling, especially when the to-be-exchanged quantities of matter are in moderate concentration.

An example is the cold temperature exchange concurrent with the exchange of matter between raw gas and purged gas in a cold temperature regenerator.

Picture 1 shows the usual regenerator arrangement of a fractionating apparatus with two equal, periodically and regularly

cycled with storage mass filled regenerator branches, together with the cycling components whose operation is schematically shown. The operating condition before cycling is shown by the solid arrows, the operating condition after cycling by the dashed arrows. The diagonal bar drawn into the upper and lover schematically shown cycling component connect after every 90° rotation the inlet respectively the outlet lines for the in and out going gas, each time with the other branch of the apparatus. The raw gas with the condensible impurities enters the left regenerator at about 25° C in the illustrated cycle, gives off its condensible parts through condensation to the storage which had been cooled before and leaves through the upper cycling component as clean gas with low temperature (i.e., minus 150°C) to be passed on to the fractionating apparatus. At the same time, clean purged gas, i.e., a fractionation product, flows through the upper cycle component into the right storage at minus 155° and flows out at the lower cycling component at about 20° loaded with the impurities which it collected through evaporation. The temperature course of a particle of the gas along the storage mass in the regenerat as it adjusts itself in its stead condition at the end of the raw gas period respectively at the end of the purge gas period, in other words shortly before the cycling, is shown in principle by a diagram in Picture 2.

The gas that reaches the storage mass shortly before the cycling changes its temperature initially only very little at the beginning layer of the storage mass, because this layer has already adjusted its temperature during the prior inflow to that of the constant temperature of the incoming gas. Only further down the mass the temperature of the raw gas falls off, respectively that of the purge gas climbs. At all other times, between the two cycles, the temperature lines of the flowing gas stay between the fat dashed and solid lines, whereby the points lying on both curves vertically below and above one another represent the two temperature extremes at any cross section of the storage mass. The temperature of the storage mass itself movestalso between these two curves. Its mean temperature is constantly in the steady condition, corresponds to the dot-dash curve. One characteristic of the regenerator operation is this constant temperature slope in the storage mass which is dependent upon the type and quantity of the mass as well as the temperature condition and the composition of the raw and purge gases.

If the raw gas contains condensible components then at a given point in time, which depends on respective operating conditions, and in a certain area of the storage mass condensate will be separated from the raw gas on one hand and on the other hand evaporated into the purge gas in a quantity that can be calculated in advance, because to each temperature belongs a specific saturation pressure of the condensible part. At specific temperature differentials in the area of saturation a certain amount of condensate will always be knocked out in the "to-be-warmed" regenerator; respectively will be evaporated in the "to-be-cooled" regenerator. At the same time a given amount of condensation heat is released on one hand respectively required

on the other hand. This positive respectivley negative, temperature tint superimposes itself on the normal energy exchange between the latent temperature content of the purge gas on one side and the raw gas on the other side, with the storage mass as the exchange medium, which stores the positive as well as the negative temperature tint initially, to pass it on to the other gas type after cycling. The advantage of this kind of energy and matter exchange, compared with the usual cleaning and fractionating processes where the condensation of a multicomponent gaseous mixture often has to take place at a lower temperature than the evaporation, is that the evaporation of the condensate in the stream of the purge gas and the fractionation products occurs at about the same or even at a lower temperature level than the condensation, whereby an approximate reversible operation is achieved.

The heat which is released during condensation is substantially taken up by the storage masses, however, remainders pass with the raw gas to zones of lower temperature. Also the cold that is being released during evaporation is carried in part to zones of higher temperature and contributes undesirably to the increase in the temperature differential at the extremes of the heat exchanger which (the temperature differential) in the interest of good heat exchange should be kept as small as possible. This happens particularly when considerable quantities of condensate are knocked out and are again evaporated.

# Exchange of Energy and Matter in Adsorbers Combined with Regenerators

The previously described process of gas treatment in regenerators is now compared with one in adsorbers, whereby the adsorbers are combined with the regenerators and are operated in a certain manner. These processes which are an interesting parallel to the prior described process shall be identified as Sorbogen Processes. A combination is shown in Picture 3.

# Sorbogen 1 Process

In the combined two-branch apparatus which has an inflow of raw gas, respectively purge gas, of about the same temperature and which consists in each branch of a cold storage, the adsorber, and the heat storage, without external influence, solely due to the positive temperature tint of the adsorption process and the negative temperature tint of the desorption process, the temperature curve in the adsorber establishes itself so that the temperature from the inlet point of the raw gas to the outlet point increases. From this it is self-evident that the storage at the raw gas side has taken on the function of a cold storage; the storage on the clean gas side, the function of a heat storage.

Per Picture 4, at the free end of the storages, temperatures differ onlyslightly from the surrounding temperatures and vary only in close limits. The temperature of the particle of raw gas flowing at ambient temperature into the cold storage therefore initially

drops in the cold storage, rises again above the ambient temperature in the adsorber, to be cooled down again to the ambient temperature along the layers of the heat storage.

In Picture 4, the temperature course of the gases in the two branches just before cycling is shown. For simplicity sake here and in Picture 8, the part of the constant temperature curve was left off (see Picture 2).

Through regular cycling, within certain time limits, one assures that the temperature gradient is maintained in the adsorbers as well as in the storages. The particle of purge gas which desorbs the adsorber after cycling is subject, as evident, contrary to the raw gas to which it flows in opposite direction, first to a temperature rise at the heat storage, then a temperature drop along the layers of the adsorber, followed by a warming to ambient temperature at the cold storage at the other end of the adsorber.

The adsorption heat that is released during the binding of adsorbable components is carried along a certain stretch by the clean gas in the direction of the flow of the raw gas. A part of the heat remains on the adsorbent itself, as it also has a certain heat storage capacity: the rest is taken up by the storage mass.

Vice versa during desorption of the adsorbent corresponding cold quantities are set free, respectively, heat is being bound which is taken in part from the adsorbent mass and in part from the gas itself. Thereby the temperature can sink considerably below the embient. The cold produced during desorption does not remain entirely on the adsorbent, but is carried in part to the cold storage by the purge gas, where the purge gas, which is loaded with desorbate, is again brought up to the ambient temperature.

The larger the adsorbed quantities, the larger is not only the development of heat during adsorption, but also the cold production during desorption. The storage masses at the end of the adsorption layers take care that the heat tint of the adsorption process which otherwise would have to be carried away by cooling water and eliminated, for example, is now usefully available to the opposite desorption process, which up to now was supported by heating.

If one replaces at each end of the adsorbers, the storage with tubular heat exchangers, one accomplishes the same thing. In this case, the cycling components are located between the continuously operating exchangers and the adsorbers, Picture 5.

The previously proposed arrangement of the adsorbent in the pipes of the heat exchanger and the adsorbing and desorbing therein is not likely to have the effectiveness of the above arrangement.

# The Principle of Partial Loading and Partial Unloading

That this process of loading and unloading of the adsorbent can also be approximately reversible regards the purge gas consumption and at the same time, achieves a high degree of purity, can be attained through two operation principles in the adsorption respectivel desorption of the adsorbent. Let us call them here, the principle of partial loading and partial unloading.

That with the inflowing raw gas, the adsorbent is not loaded to saturation, but only to a breakthrough value, has been known for a long time. (Breakthrough value is the loading value of the adsorbent at which the component that is to be removed from the inflowing gas, appears in the outgoing clean gas.) If one, however, wishes to obtain a high degree of purity, the loading of the adsorbent to nearly its breakthrough value is still too high.

In accordance with the new principle of partial loading, the adsorbent is only loaded to a fraction of its breakthrough value and the adsorption is then interrupted. In this way a relatively large layer of the adsorbent remains entirely unloaded, which is acceptable, as it is the characteristic of the described process and arrangement to allow a more frequent cycling.

Through application of this principle, surprisingly high purity of air was achieved in a technical installation, as later described, also with relatively difficult adsorbable impurities like CO2, at a temperature, which up to now was considered unsuitable for this purpose, additionally when at the same time the heating of purge gas was omitted and the still to be described principle of partial desorption was utilized. Requisite for the highest degree of purity is, of course, that the purge gas be entirely free of the components to be removed and always flows in the same direction over the adsorbent which is opposite to the raw gas flow. The principle of partial desorption (unloading) is based on the consideration that a complete unloading of the adsorbent would require too large a quantity of purge gas to make it most eager for the following period of adsorption

The working principles are explained in Picture 6, which is based on measurements performed some time ago in the laboratories of the Gessellschaft fur Linde's Eismaschinen and about which will be reported later. It was found that at an ambient temperature (20°C) reported later. It was found that at an ambient temperature (20°C) reported later air of its impurities, among others also of the with the could clean air of its impurities, among others also of the with difficulty adsorbable carbon dioxide, with a purity in excess of 99%, using a layer of 1.5 m of activated charxoal, of 1 to 2 mm of grain, starting with a CO<sub>2</sub> residual loading of 8% of the saturation value, and then subsequently, at about the same temperature, purging with a value of about three times of purge gas in counterflow to the residual value of about E% partially unloaded.

Picture 6 shows on the absissa, the length of the layer in fraction of the whole, and on the ordinate, the relative loading height of the vertical cross section (the adsorbent is pictured as lying horizontally) in fraction of maximum saturation loading. The two S forming lines are the loading fronts which are enclosing the so-called add-load zone Z. The left front deliniates the area of the permanent load, respectively residual load, the right front, the one of the add-load at the moment of cycling to the counterflow unloa ing. Between this S forming load front on the right and the end of the lover line the unloaded ware. This and similar measurements will layer lies the unloaded zone. This and similar measurements will be reported in a later article. Because the purge gas in counterflow to the raw gas streams at the end over the adsorbent layer which is constantly saturated, it loads itself up with desorbable components to the maximum until the close of the purge gas period. The purg ng is stopped when the loading of the purge gas drops off substantia ly. One can figure an isotherm partial adsorption and desorption at the same total pressure with about three times the purge gas volume if one wants, at the same time, maximum cleaning effect. With twice the purge gas volume, the cleaning effect drops off some. At each 5°C higher purge gas temperature, the ratio of purge gas to raw gas volume is cut in half, so that at 10°C higher temperature one already needs less purge gas than raw gas. It is a matter of planning to coordinate the requirement for good utilization of the available purge gas with the requirement for a good heat exchange. It is always possible to exceed the guide figures by fractions, so that one can do justice to both requirements which do not contradict each other.

The situation that with isotherm desorption, one needs several times the purge gas than the raw gas volume, in spite of this economical working method, shows that one has to figure with a cortain hysteresis. Apart from the fact that one cannot expect complete equilibrium between adsorption phase and gas phase, the excess consumption on purge gas has to do with the temperature depression, which occurs during the desorption of the adsorbent in the last jurged and still heavily loaded adsorbent layer. In the laboratory scale, that is with a large surface compared to mass and good heat transfer, this effect is hardly noticeable; in technical installations, however, it could be clearly observed. The arrangement of the storage masses at the end of the adsorbent layer causes that this effect does not work out to a disadvantage. As a consequence of the partial unloading principle, the retained load in the adsorbent along the retained load front prevents the adsorption heat during adsorption from concentrating in a small space, but distributes it over a greater distance, whereby the above mentioned climbing temperature curve towards the adsorbent end and a better thermic effectivenessare achieved. Vice versa in a fully described adsorbent, a large amount of heat would become free in a small space, which considering the reversible operation would be especially disadvantageous, if as in the Sorbogen II Process (Picture 7) for special reasons the temperature gradient along the accordent layer is increased through heating respectively cooling

apparatus between exchangers and adsorbers to bind and eventually enrich the volatile impurities respectively gas components.

### Sorbogen II Process

Here, a cooling apparatus at the raw gas inlet, i.e., between the cold storage and the adsorbent, respectively, a heating apparatus at the clean gas outlet, i.e., between heat storage and the adsorbent, is arranged. This system allows to heat and cool both branches constantly, and at the same time. Thereby, time is gained for precooling, respectively preheating, of the storage masses which are precooling the ray are respectively probabiled. precooling the raw gas, respectively preheating, the purge gas. The mutual influencing of heating and cooling apparatus is prevented through regular cycling and maintaining of a temperature curve along the adsorbent layer. Depending on the flow condition in the prevailing cycle, the cooling apparatus either cools the raw gas before its entry into the adsorbent or after cycling the outgoing loaded purge gas before it enters into the cold storage, which now after its temporary partial warming by the raw gas, is being blown cold again (Picture 7). During one period, the heating apparatus heats the purge gas which has been preheated by the heat storage before it goes into the adsorbent. During the following period, it (the heat apparatus) heats the purified gas before it goes into the adjoining precooled heat storage. The heat storage can therefore, after cycling, preheat efficiently the purge gas. Of course, also in this arrangement the adsorbents and storage masses are kept in a constantly maintained temperature curve, whereby the free end of the storage is always near the ambient temperature (Picture 8). Here also, (again) the change of the temperature of a particle of raw respectively purge, gas flowing through the apparatus shortly before cycling is schematically shown. Under the influence of heating and cooling the temperature curves of raw and purge gas cross over. The dot-dash line again shows the course of the mean temperature of the adsorbent, respectively the storage mass. Advantageous in this arrangement/the reinforcing of the heating effect by the adsorption heat carried towards the adsorbent end and the reinforcing of the effect of the cooling apparatus by the desorption cold carried towards adsorbent start. Also this arrangement enables a nearly reversible operation down to the area of very low temperature with a corresponding steep temperature curve. As we already mentioned above, an excess of purge gas over raw gas is no longer needed at a temperature increase of 10°C.

If one wishes to recapture the adsorbed gas components, a further increase of the temperature difference with concurrent reduction of the purge gas volume is adequate. An additional possibility of enrichment exists in the expedient desorption at sub (lower) pressure and, in the sense of the above execution, by maintaining a counterflow perge. In these circumstances, one can also use as purge gas, a pertial flow of the clean gas branched off downstream from the adsorbent. The use of a moderately higher pressure, i.e., 2-10atm., during the adsorption of the adsorbent is advantageous in case the cleaned

gas shall be available under pressure. At higher pressures, the gas losses increase at cycling under certain circumstances beyond an acceptable figure as also part of the cleaned gas is adsorbed and is lost during the pressure reduction at cycling. The technical utilization of Sorbogen I Process, as well as the preparatory experiments for it, will be reported in a following later article.

### Summary

The process and apparatus prerequisites for an approximate reversible operation (called Sorbogen I Process) in the cleaning of gases through adsorption with relatively short duration cycling of the adsorber, preferably for the purpose of further fractionating of the cleaned gas under elevated pressure and at lowered temperature, are explained. Due to the similarity of the cycling operation as well as the thermal and matter exchange characteristics, the process is being compared with the process of gas purifying by means of cold generators.

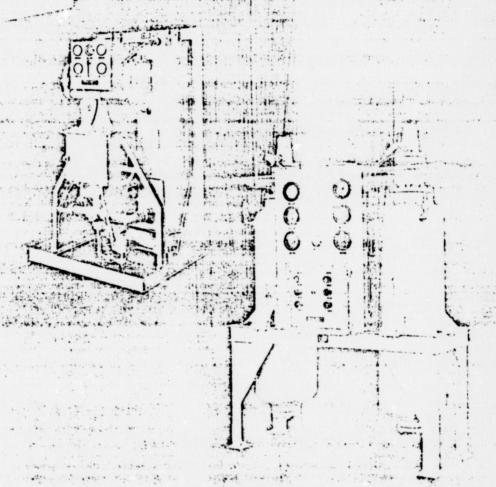
On hand of schematics, drawings and diagrams, the principles of "reversible" operation, namely the heat exchange between adsorption (loading) and desorption (unloading) process, even without use of foreign heat and cooling sources, are explained. A condition to achieve a maximum purifying effect even in the removal of difficult to adsorb impurities is the maintaining of a very large free (unloaded) zone. This is called the principle of "partial loading". A "reversible" operation is promoted through use of the principle of "partial loading". The known and always consistently applied purge degasing with clean purge gas in counterflow to the raw gas is a further prerequisite for the highest purity effect as well as for "reversible" operation. The work method for corichment and gaining of the adsorbable components (called Sorbogen II Process), utilizing the same principles and with most economical use of energy for heating and cooling together with the prerequisites of the apparatus for it, are given.

# Submitted August 11, 1952 and

- 1) Desch. Patentann. G 6724 IV b/12e.
- 2) Disch. Patentann. P 22 720 IV b/12eD.
- 3) Disch. Patentania. G 405 IV b/12e
- 4) Disch. Patentanm. G 94 IV b/12e:

# PLAINTIFF'S EXHIBIT 6A

Trinity Equipment Corporation Bulletin A-309



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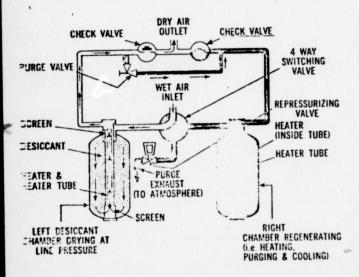
# TRINITY TYPE A HEAT R

Trinity Type A Dryers are designed to provide a dependable source of dry air or gas with dewpoints down to -100°F. The standard parkages as described on the opposite page are all automatic. (Semi-automatic and manual units are available on special order.)

These dryers use no blowers, utilizing the principle of atmospheric regeneration whereby a small percentage of the effluent dry gas is introduced into the chamber undergoing regeneration and then passing out through the purge line. Electric heating units are employed in the desiccant chambers to raise the temperature of the bed during the reactivation process. Cycling time is adjustable to meet the specific needs of the installation, with the usual cycle time of 6 hours. Steam heated units are available on special order.

Trinity Type A Heat-Reactivated Desiccant dryers are of an advanced design, carefully engineered and manufactured to provide the finest performance, greatest dependability and lowest operating costs.

#### TYPICAL FLOW DIAGRAM (3COA to 875A)



GAS BEING DRIED PURGE GAS (FOR REACTIVATION)

A typical flow circuit for Models 300A through 875A is shown above. The smaller Type A models have flow circuits based upon a similar principle. Each Type A dryer utilizes a small dry-air counter-flow purge which exhausts to atmosphere. Models 50A and larger include repressurization of the chamber being reactivated, before cycling switchover.

# **FEATURES**

 Exclusive air-flow heater tubes prevent channeling during drying and provide better heat conduction into the bed during reactivation. (Models 25A through 875A)

Electric heaters do not contact desiccant bed and may be removed and reinserted without disturbing the bed.

(All models)

 Flow of purge is counter-current to the drying flow. Purge is pre-dried. (On models 25A through 875A purge is preheated)

 Repressurizing valve on drain eliminates hammering, or moving action of desiccant, resulting in longer desiccant life. (Models 50A through 875A)

# USED AND APPROVED IN MUNDREDS OF INSTALLATIONS

Trinity Type A Heat-Reactivated Dryers are currently in use in industrial, scientific and commercial operations throughout the world. Many of these units have been in service for periods of over 10 years and have established significant records for economy, dependability and permance.

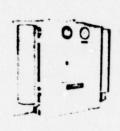
Widely used as a means of drying instrument air, Trinity dryers have also found such diversified uses as drying air or gas for food and drug processing, atmospheric furnace purging, electronic transmission line purging, drybox assembly purging, and drying process gases.

### HOW IT OPERATES

(Operation of Models 300A through 875A is described)

Air or gas enters through the four-way valve and passes into the left-hand chamber. The air or gas then passes through the desiccant bed which adsorbs the moisture. The driedgas then goes through the heater tube, through the open check valve, and out into the system. A small percentage of the dried gas passes through the purge valve to the chamber undergoing reactivation which has been dropped to atmospheric pressure. The purge is pre-heated as it passes over the heaters, and carries off the moisture in the desiccant bed out through the purge exhaust valve. At the end of the heating cycle, the heater is de-energized and the right chamber cools. Before the end of the cooling period, the purge exhaust valve closes, permitting a build-up of pressure in the reactivated chamber to line pressure. This repressurization eliminates surges downstream of the dryer and bed movement on switchover. At the end of the cycle, the switching valve directs the gas into the right chamber and the purge exhaust valve opens and the left chamber is reactivated.

# EACTIVATED DRYERS



#### TYPE A MIDGET DRYER

Models 5A-EIA6, 10A-EIA6, and 25A-EIA6. For drying small flows of com-pressed gases in instrument air, inert gas and purging systems.

"A" PACKAGE

FEATURES

**Outlet Pressure Gauge** 

DRYER NO.

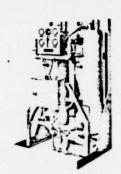
5A-EIAS-A1

10A-EIA6-A1 25A-EIA5-A1

625A-EIA6-A1

7504.FILS.A1

875A-E1A6-A1



#### TYPE A MODELS 50A-EIA6 TO 200A-EIA6 DRYERS

Floor-mounted units designed to dry intermediate volumes of compressed air or gas for industrial and laboratory purposes.

"B" PACKAGE

FEATURES

Visual Moisture Indicator

Chamber Pressure Gauges

Chamber Thermometers

Purge Flow Indicator Visual Moisture Indicator

**Outlet Pressure Gauge** 

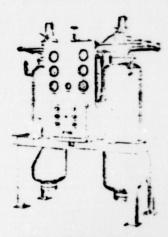
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DRYER NO.

5A-EIA6-B1 10A-EIA6-B1 25A-EIA6-B1

7504.FIA6.R1

875A-EIAG-B1



1/2

#### TYPE A MODELS 300A-EIA6 TO 875A-EIA6 DRYERS

Large capacity to meet the ever-in-creasing needs of industry for sub-zero dewpoints in air or gases.

Trinity offers a complete line of standard Type A Dryers in the most popular sizes. These standard models are offered in two basic packages. Package A dryers include the basic minimum instrumentation necessary for proper operation, and Package B dryers include deluxe instrumentation for additional operating information.

To meet special requirements, the Trinity engineering staff will modify any of these standard units. Consult your local Trinity sales representative, or the Trinity factory for complete information on specials.

#### 50A-EIA6-A1 100A-EIA6-A1 50A-EIA6-B1 100A-EIA6-B1 **Panel Mounted** Locally Mounted Chamber Pressure Gauge Purge Flow Indicator Visual Moisture Indicator Chamber Pressure Gauge 150A-EIA6-A1 200A-EIA6-A1 Locally Mounted 150A-EIA6-B1 **Panel Mounted** Chamber Pressure Gauges Chamber Thermometers Purge Flow Indicator Visual Moisture Indicator Chamber Pressure Gauge 200A-EIA6-B1 Panel Mounted 300A-EIA6-A1 Locally Mounted 300A-EIA6-B1 Inlet Pressure Gauges Outlet Pressure Gauges Chamber Pressure Gauge 400A-EIA6-B1 500A-EIA6-B1 625A-EIA6-B1 400A-E1A6-A1 50CA-EIA5-A1

DISTINGUISHING FEATURES OF STANDARD PACKAGED UNITS

The above NEMA 1 dryers can be supplied in either NEMA 4 or NEMA 7 electrical construction by specifying Package A4 or B4 (for NEMA 4) or Package A7 or B7 (for NEMA 7)

Standard pressure: Models 5A to 25A-30 psig min., 150 psig max. (Not code stamped) Models 50A to 875A—50 psig min., 150 psig max. (ASME code stamped)
Standard temperature: 40°F. Min. to 120°F. Max.
Electrical Requirements: 5A through 25A—115 Volts. 60 Cycles, 1 phase

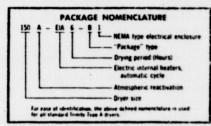
50A through 150A-115 Volts or 230 Volts, 60 cycles, 1 phase 200A-230 Volts, 60 cycles, 1 phase

300A through 875A-230 Volts, 440 Volts, 550 Volts, 60 Cycles, 3 phase

FILTERS: It is normally recommended that a suitable prefilter be installed ahead of each dryer to assure the most efficient operation. Also, when the usage so dictates, an appropriate afterfilter should be used after the dryer. Trinity offers a complete line of filters.

#### HOW TO ORDER

Sizing information is provided on the back page of this bulletin. Trinity also maintains field sales and engineering offices throughout the country, staffed by competent personnel experienced in sizing and specifying the dryer best suited to your individual needs. These services are available to you...



# SIZING INFORMATION

#### How to size a dryer:

1. Calculate the water load

W = KV W = Water load per drying period (lbs.)

K = Sizing factor (See Table II)

V = Volume of gas being dried (SCFM)

 Select a tentative dryer size from Table I. The selected dryer must have a "W" capacity equal to, or greater than, the calculated value. 3. Velocity Check

U = Chamber velocity (ft./min.)

14.7 V

P = Inlet pressure (psig)

A = Chamber area (sq. ft., see table I)

Note: If the calculated chamber velocity exceeds 45 ft./min., change the selection to a larger model that will provide a velocity of 45 ft./min. or less

DRYER SIZE	SIZE CONNECTIONS (INLET & OUTLET)	DIM	ENSIONS (APPR	ROX.)	PURGE VOLUME (SCEM)	APPROX. SHIPPING WEIGHT (LBS.)	NOMINAL WEIGHT OF DESICCANT PER CHAMBER (LBS.)	CHAMBER AREA "A" (SQ. FT.)	WATER LOAD* CAPACITY (LBS.)	ELECTRICAL DATA	
		Height	Width	Depth						DEMAND (KW)	CONSUMP TION PER DRYING PERIOD (KW-HR)
5A	14" NPT	1.9-	2.3	5%"	0.2	135	3	0.041	0.36	0.125	0.5
10A	14" NPT	1.9-	2:-3"	5%	04	155	5	0.087	0.6	0.150	0.6
25A	45" NPT	2.6	2.6	814"	1 1	250	121/2	0.125	1.5	0.5	2
50A	1" NPT	4.3	2.0	2.2	7 2	850	29	0.15	3.0	1	4
100A	142" NPT	4:3	2.0	2.2	3	1000	47	0.305	4.8	2	7
	142 NPT	5.0	2.9	2.9"	1 4	1350	97	0.5	10.2	3	11_
150A	CONTRACTOR OF STREET,	5.0	2.9	2.9	1 5	1550	125	0.78	13.2	4	14
200A	142" NPT	6'-10"	4:71/2"	2.314"	10	2500	190	0.9	23	142	18
300A	2" NPT			2.414	12	2750	280	1.2	34	71/2	21
400A	2" NPT	6-11	4:111/2	2.514	15	3050	375	1.74	45	742	27
500A	2" NPT	7:-1"	5:31/2"	2.9	20	3300	440	2.1	53	12	33
625A	3"†	7:5	5'.742"		25	3650	570	2.35	68	12	40
750A	3"+	7:-8"	5:-11:45	2:-11"	30	3900	640	+ 31	78	12	45
1 875A	3°†	7'.8"	6.31/2"	31.	30	3300	1 340				-

13"-- 150 = FLANGED INLET

"WATER LOAD FOR SORBEAD OR SILICA GEL FOR H-151 ACTIVATED ALUMINA MULTIPLY "W" by 0.84 FOR F-1 ACTIVATED ALUMINA MULTIPLY "W" by 0.42

			15.1	14: 1	57	Hele	5440	101				
PSIG	30	40	50	60	70	80	90	100	110	120	125	150
50.	061	050	042	036	032	.029	026	024	022	020	020	.017
60.	099	.081	068	059	052	047	042	.038	.035	.033	.032	.02
70	139	114	096	084	074	066	.059	054	.050	046	045	038
80	194	159	134	116	103	1 092	.083	.075	.069	.064	.063	.055
90.	266	218	185	160	141	1.126	1114	.104	.096	.088	.085	.075
100. 1	365	297	252	218	192	1.172	1.155	141	.130	.121	.116	.09
105.	425	345	295	255	225	200	1.180	164	.151	.140	.136	.11
110	490	400	340	293	.258	230	208	1.179	.167	161	.157	13
115	562	460	388	337	297	266	240	218	202	.186	181	1.15
120	646	530	446	.387	342	305	274	250	231	.213	.207	16

DEFINITIONS ACCORDING TO NEMA STANDARD AD-1-1959 CYCLE is the time allowed for a desiccant bed to be in drying service, reactivated, and returned to drying service. A DRYING PERIOD is the portion of a cycle during which the desiccant bed performs the drying function. STANDARD CUBIC FEET PER MINUTE (SCFM) is the flow rate which, for convenience, has been referred to standard conditions (A temperature of 70°F and at an atmospheric pressure of 29.92 inches as measured on a mercury barometer.)

MOTE: Above table of "K" factors is based upon 6 hour drying period. Multiply "K" by 1.33 for an 8 hour drying period.

OTHER



# **PRODUCTS**

# TYPE AB DRYERS

Blower-type dryers for use where no cooling water is available, or in intermittent or low-flow applications. See Bulletin AB-310.

## HEAT-LES DRYERS

An exclusive Trinity design using no heat for regeneration and for extremely low dew point. Low initial and operating costs. See Bulletin HA-308.

#### UNITIZED DRY-AIR SYSTEMS

Completely packaged, readyto-operate systems including compressor, dryer, accumulator, and instrumentation. See Bulletin CD-138.

#### FILTERS

Trinity offers all types of prefilters and after-filters to meet specific requirements.

ALSO THERMOWELLS, THER-MOCOUPLES, AND SELF-SHEATHED THERMOCOUFLE ASSEMBLIES



TRIMITY EQUIPMENT CORPORATION,

A Subsidiary of Pall Corporation

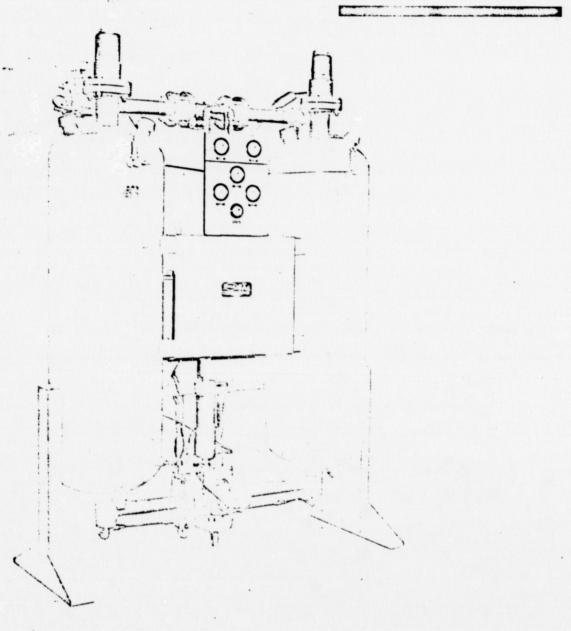
CORTLAND, NEW YORK, U.S.A.

# PLAINTIFF'S EXHIBIT 6B

Pall Trinity Micro Corporation Bulletin A-309B









PALL TRINITY WICRO CORPORATION
A SUBSIDIARY OF PALL CORPORATION

CORTLAND, NEW YORK 13045, U.S.A. • TEL: 607-756-7535 • TWX: 510-252-0791 • CABLE: TRINCORT

# TYPE A HEAT-REACTIVATED DRYERS

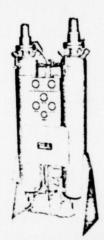
# 15 STANDARD MODELS WITH INDUSTRY'S WIDEST SELECTION OF OPTIONS



#### TYPE A MIDGET DRYER Models 5, 10, and 25

Wall mounted units for drying small flows of compressed gases in instrument air, inert gas and purging systems. Standard units supplied with outlet pressure gauge.

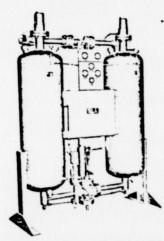
Unit shown - Model 25AE1 -00000A



#### TYPE A Models 52 to 252 DRYERS

Floor mounted units designed to dry intermediate volumes of compressed air or gas for industrial and laboratory purposes. Standard units are supplied with relief valves, chamber pressure gauges and thermometers, and purge flow indicator.

Unit shown - Model 52AE1 -00000D



## TYPE A Models 302 to 877 DRYERS

Large capacity to meet the everincreasing needs of industry for subzero dewpoints in air or gases. Standard units supplied with relief valves, chamber pressure gauges and thermometers, and purge flow indicator.

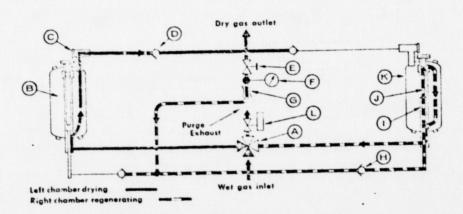
Unit shown - Model 402AE7-00000D

# TYPICAL FLOW CIRCUIT (Models 302AE & Larger)

Wet gas enters the 4-way inlet switching valve (A), passes up through the left desiccant bed (B), through the stainless steel cleanable outlet filter (C), and outlet check valve (D) to the dry gas outlet.

A small portion of dried gas passes through the purge throttling valve (E), purge indicator (F) and purge flow orifice (G) which controls the flow rate. Metered purge then passes through the right purge flow check valve (H) up through the heater tube (!) and over the electric heater (J). Heated purge then enters the plenum area of the chamber (K) where it is dispersed downward through the

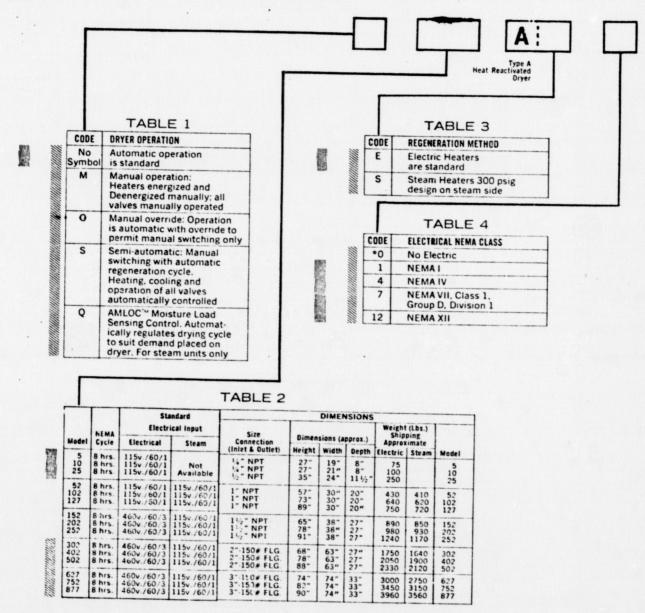
wet desiccant bed in a direction counter-current to the drying flow. The purge gas, now carrying previously adsorbed moisture, exits to atmosphere through the 4-way and purge exhaust valve (L). Shortly before end of the cooling period, the purge exhaust valve classes to repressurize the reactivated chamber. Switchover takes place with both chambers at line pressure, eliminating desiccant bed attrition, displacement of switching valve lubricant and line surges. The left chamber is then exhausted to atmosphere and its regeneration cycle initiated, while the fully regenerated right chamber dries gas at line pressure.



# MUDEL SELECTION CHART

PTM Provides Design Versatility — This chart contains our standard dryer sizes as indicated in Table 2. The remaining tables cover all of the options which can be included with each model number. Thus, once the proper model number is selected, (based on operating conditions) a dryer can be chosen with all the options needed for your requirements. Complete design flexibility is provided by selection of the type of dryer operation, regeneration method, electric NEMA class, NEMA cycle, electrical input design pressure, instrumentation, alarms, and chamber insulation. An illustration of the procedure is shown below.

While the chart offers a ready reference to the systems available on standard order, PTM dryer specialists are ready to work with you in developing the optimum equipment for your requirements . . . and to custom engineer a system to fit.



#### EXAMPLE

To designate the desired dryer, the code numbers should be inserted in the proper boxes at the top of the chart. Therefore, Dryer Model 127 could be:

Table 1 Table 2 Table 3 Table 4 Table 5 Table 6 Table 7 Table 8 Table 9 Table 10

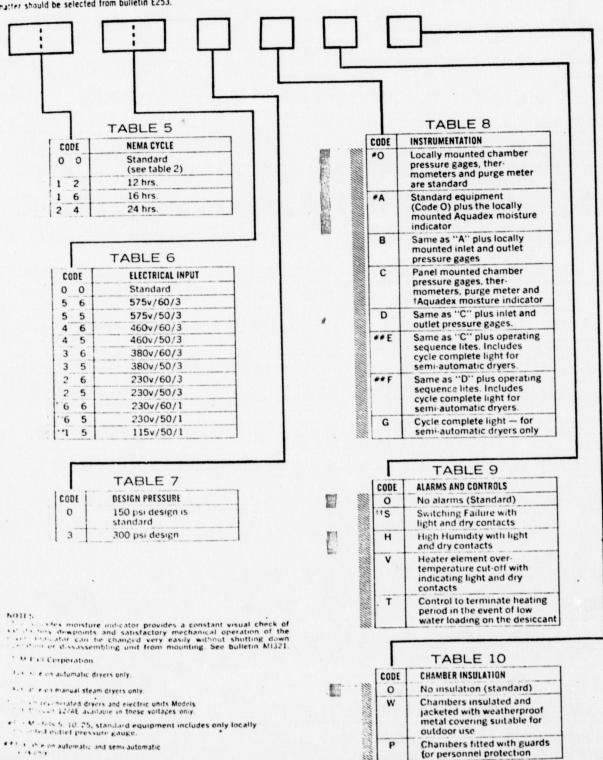
This would be an automatically operated model 127; steam-heated, NEMA 1 electricals, standard 8 hr. NEMA cycle, 115v.: 60-1 electrical input, 300 psi design, standard instrumentation (see Option 0) Table 8, plus the locally mounted Aquadex\* Moisture Indicator, switching failure alarm with indicating light and dry contacts, and no insulation.

All zeros following last option can be emitted.

# ORDERING INFORMATION

the chart is pattern coded because of the many alternatives available. the model number is selected from Table 2, the accompanying pat-ty the same pattern code can be selected. For example, Model 127 \_\_\_ Thus, every option is available to this unit. is coded

Prefilters and after-filters to eliminate oil contamination and particulate matter should be selected from bulletin E253.



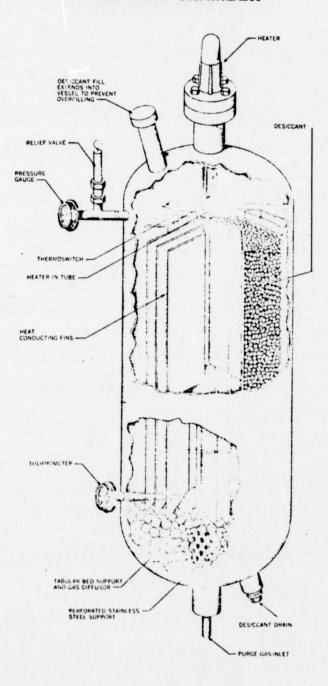
for personnel protection

# EFFICIENT-AUTOMATIC-LOW MAINTENANCE

Heated type unit with upflow drying. Heating and cooling are counter-current with dry air purge to atmosphere. Heaters are internal. Partial cooling is provided by radiation and convection. Units feature advanced design for maximum drying efficiency and minimum purge gas usage. May be operated on intermittent flows from 0 to maximum rated capacity. No blower or cooler is required, thus reducing operating and maintenance costs.

PTM Heat-Reactivated dryers are used to supply dry instrument air, process gases, blanketing gases, control air for waveguide purging; in any system requiring a dependable low-cost source of dry air or gas.

# TYPICAL ELECTRICALLY HEATED DESICCANT CHAMBER



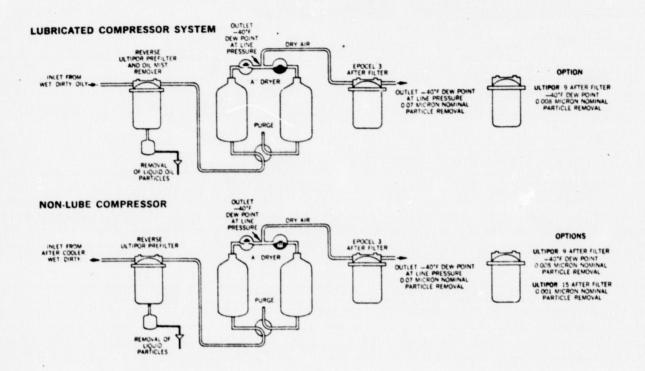
#### **FEATURES**

- 1. Counter-current preheated dry gas purge provides maximum removal of adsorbed moisture with minimum gas loss.
- 2. Unique finned heater tubes effectively conduct regeneration heat throughout the entire desiccant bed and prevent localized hot spots and element damage common with imbedded type heaters.
- 3. High efficiency Incoloy-clad heater elements are furnished.
- 4. Internal heaters are used to minimize heat loss.
- 5. Heaters are not in physical contact with desiccant, hence: a) May be serviced without disturbing the desiccant bed. b) No desiccant breaking due to contact with high sheath temperatures. c) No possibility of ignition of oil-soaked desiccant.
- 6. Adjustable thermo switches maintain proper bed temperatures. (Models 52 and larger)
- 7. Standard on Models 302AE through 877AE are heaters electrically interlocked with the valve switching mechanism to prevent heaters from energizing in the event of switching failure. This is independent of other alarms or interlocks which may be provided as optional equipment.
- 8. Repressurization circuit is included as standard equipment. This allows raising the regenerated desiccant chamber to full line pressure gradually before switchover which: a) Eliminates desiccant attrition by preventing bed movement. b) Prevents displacement of the switching valve lubricant by equalizing pressures across the valve during switching. c) Avoids line surges downstream of the dryer.
- 9. Separate desiccant drain and fillports are provided as standard equipment on larger models. This: a) Eliminates the need to disconnect the piping or wiring when recharging the dryer. b) Permits recharging without disturbing the electrical heating elements. c) Automatically limits the bed height to guarantee plenum area necessary for a uniform inlet air flow profile through the desiccant bed and for proper purge gas dispersion.
- 10. Removable stainless steel outlet filters are provided on models 302 and larger to prevent small particle carryover. These filters may be removed for cleaning without disturbing the desiccant bed.
- 11. A stainless steel support is provided in each chamber to retain the desiccant and diffuse the inlet flow for maximum bed utilization.
- 12. Pressure gauges, temperature gauges, relief valves, a purge air indicator and pilot air filter are supplied as standard. (Models 52 and larger)
- 13. Models 52 and larger are either U stamped or UM stamped in accordance with the requirements of the ASME, UPV code.
- 14. Special high tension electrical enclosure is provided on all dryers using voltages of 230 volts, 3 phase and over. This box separates the high voltage from the control voltage.
- 15. Standard units are designed to deliver dry gas with a  $-40^{\circ}$ F dewpoint. Dryers which produce a dewpoint as low as  $-100^{\circ}$ F are also available.

# TYPICAL INSTALLATION

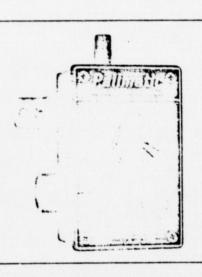
OIL CONTAMINATION AND FILTRA-TION — A prefilter and an afterfilter should be included with all dryer installations. Desiccants should be protected from contaminants such as oil, pipe scale, liquid water, foreign liquids, and dirt. PTM manufactures an exclusive pre-filter known as the REVERSE ULTIPOR filter which not only will remove 99% of all incident liquid oil but will also provide 98% removal of all solid contaminants larger than 0.04 microns! This represents a level of purity hereto-fore unobtainable.

Iso provide 98% resolid contaminants 0.04 microns! This level of purity here-



# PALLMATIC\* AUTOMATIC DRAIN VALVE

PTM now offers positive protection from flooding, often caused by faulty traps and sticking float valves. The Pallmatic Automatic Drain Valve is a compact, timer controlled solenoid operated discharge unit, designed to handle the oil-water sludges collected in system filter housings, receivers and separators. For complete information, see PTM Bulletin DV350.



TRADEMARK PALL CORPORATION



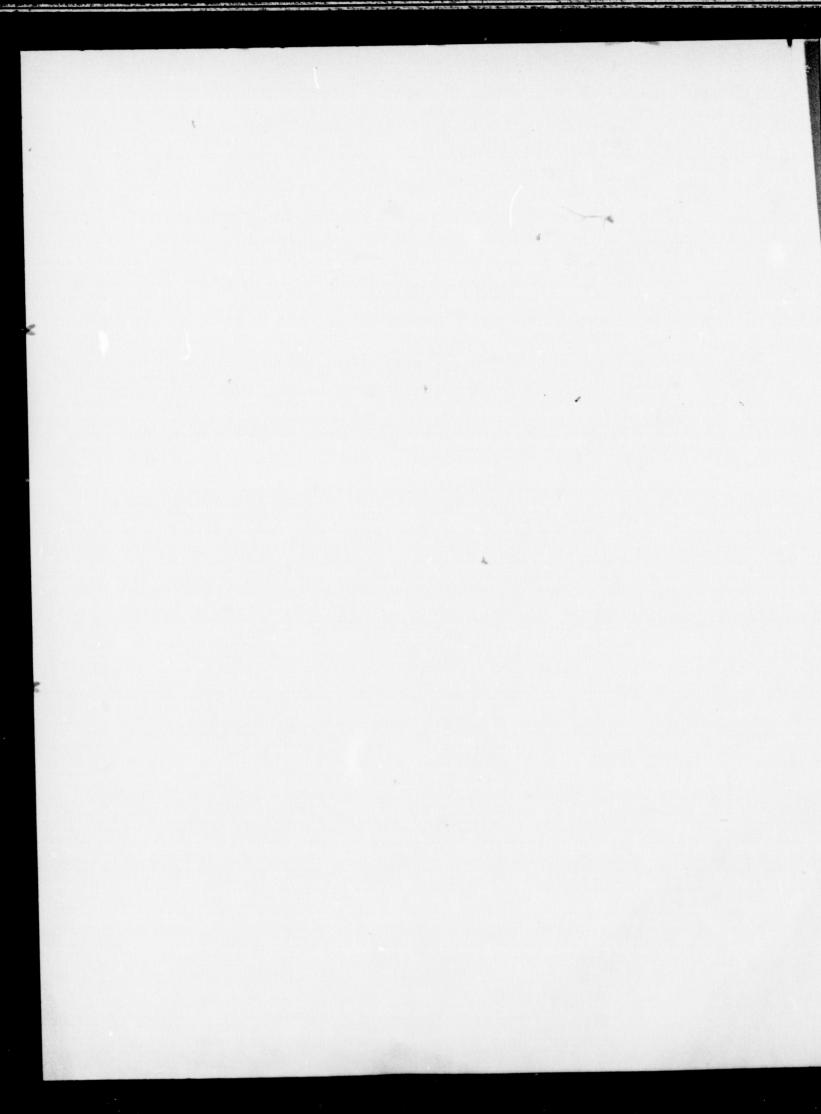
A SUBSIDIARY OF PALL CORPORATION

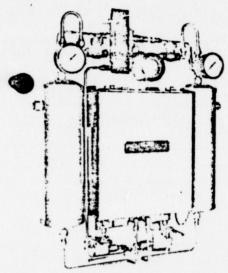
CORTLAND, NEW YORK 13045, U.S.A. • TEL: 607-756-7535 • TWX: 510-252-0791 • CABLE: TRINCORT

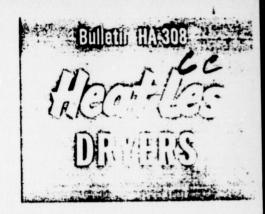


# PLAINTIFF'S EXHIBIT 60

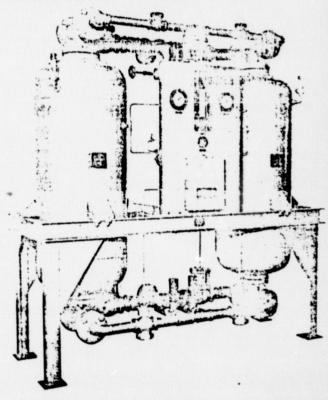
Trinity Equipment Corporation Bulletin HA-308

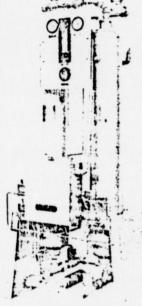






For super-dry gas and air at lower initial and operating costs





CONTRACT GOVERNMENT GOVERNMENT GOVERNMENT WAY AGON THEY

en TER

# THE CONTROL CONTROL DRYER

The exclusive design of the Trinity Heat-Les Dryer offers so many obvious advantages over the old-fashion heat-reactivated types, that it is specified in more installations than any other type today. Whether you require dewpoints far below those available with other designs, or you want optimum dependability and lowest operating costs, or again, if you have a limited budget for initial equipment—the Trinity Heat-Les is the answer.

Satisfied users of the Trinity Heat-Les read like a blue book of industry . . . leading petroleum companies, chemical processing plants, power generating stations, electronic components manufacturers, food packagers, textile plants, in fact just about every industrial area requiring dry air or gas for instrumentation or processing is using and complimenting the Heat-Les Dryer for its entirely new and better standards of performance and economy.

In addition, some of the most extensive military programs, including many of the operational missile programs specify and use the Heat-Les as a part of a Trinity Unitized Dry Air System.

### **OPERATIONAL ADVANTAGES**

Inasmuch as the Trinity Heat-Les Dryer employs no heaters, maintenance usually associated with these components is entirely eliminated. Since no heat is used, desiccant life and efficiency is greatly increased through the elimination of oil-varnishes forming on surface of desiccant particles. The Trinity Heat-Les Dryer has a normal tendency to reject oil which enters with the incoming gas. While complete oil elimination is not always positive, many users have completely solved their oil problem by proper application of a Heat-Les Dryer. The Heat-Les Dryer is the dependable, low-cost approach in the supply of super-dry gas or air.

### **FEATURES**

- Provides super-dry air or gas with dewpoints below — 100°F, at line pressure.
- Completely eliminates costly electric or steam heaters
- No increase in temperature of effluent gas
- Corrosion reduced due to low temperatures
- Lower installation costs
- Lower initial costs
- Lower operating and maintenance costs

# STANDARD MODELS

All Trinity Heat-Les Dryers listed in the following tables are standard design, pre-engineered, production models available for fast delivery. Some of the more popular models are carried in stock for immediate delivery.

In addition to the standard models offered, our Engineering Staff can modify these standard units to meet your specific requirements. Consult your local Trinity Sales Representatives, or our main office for further information.

Package "A" dryers include the basic minimum instrumentation necessary for proper operation. Package "B" dryers include deluxe instrumentation for additional operational information.

"A	" PACKAGES	"B" PACKAGES			
Dryer No.	Features	Dryer No.	Features		
2HA2-A1 3HA2-A1 5HA2-A1 10HA2-A1 25HA2-A1	Wall Mounted 150 PSI Design Locally Mounted: Chamber Pressure Gauges	2HA2-B1 3HA2-B1 5HA2-B1 10HA2-B1 25HA2-B1	Wall Mounted 150 PSI Design Lecally Mounted: Chamber Pressure Gauge Purge Flow Indicator Visual Moisture Indicator		
35HA2-A1 thru 1500HA2-A1	Floor Mounted 150 PSI Design (ASME Code Stamp)* Purge Exhaust Muffler Relief Valves Locally Mounted: Chamber Pressure Gauges Purge Flow Indicator	35HA2-81 thru 1500HA2-81	Floor Mounted 150 PSI Design (ASME Code Stamp)* Purge Exhaust Muffler Relief Valves Switching Failure Alarm (1 Light & Dry Contacts) Panel Mounted: Chamber Pressure Gauge Purge Flow Indicator Visual Moisture Indicator		

Model 35HA is not code stamped.
 Electrical Requirements: 115 volts, 60 cycle. (Note: Special voltages and cycles available on application).
 Power Consumption: 75 watts (approx.).

										(J)	ACIM	· filte	
÷	•	08758 S ZE	\$12E \$200.63	DIMEN	SICNS (APP	RCX.)	PURGE RATE (SCFM)	APPROX.	WEIGHT OF DES	CMAVBER APEA A	CHAMBER VOLUME	STYER	
0.0		3 25	, Truis	HE:GHT	WIDTH	DEPTH	AT FULL INLET CONDITION	WEIGHT	CHAMBER (LBS)	(sq. ft.)	(cu. ft.)	SEE	1* 5
		2-4	1,11,97	22-5	1814"	512"	33	70	1	.023	.02	1 234	
		3 1	1.77.77	24131	1814"	512"		70	1.65	.033	.036	3-4	
			12 577		15.4	512"	.79	3.5	23	.045	.048		
		12.	4 4171 -		19:4"	512"	1.45	90	4.40	.082	.058	10ma	
		25HA	1/2" NPT	34"	24"	9"	3.56	145	10.8	.128	.216	25itA	- 11
1		35HA	¾" NPT	4'.91/2"	2'-51/4"	1'-934"	7.4	225	22	.128	.45	35HA	3:
		50HA	1" NPT	5'-5%"	2'-544"	20.		460	40	.207	.776	5CHA	5.
		100HA	1" NPT	5'-5%"	2'-51/4"	20.		650	67	.347	1.334	100HA	83
		150HA	11/2" NPT	5'-101/4"	3'-4"	2'-4"		990	104	.547	2.084	150HA	139
:		200HA	11/2" NPT	5'-1014"	3'-4"	2.4"	43	1235	147	.785	2.95	200HA	200
-		T 300HA	2"-150= Fig+	6:-134"	4'-712"	1'-91/2"	53	1720	163	.94	3.66	300HA	25
		4)144	2"-150= Fig+	6'-2-4"	4'-1!12"	1'-1112"		2100	247	1.28	4.94	Engh4	-3.
·	- 1.		2"-150= Fig-	6'-5'	5-342"	2.115	89	2700	316	1.60	6.33	550.44	-
1 - 1 1		625MA	3'-150= Fig+	5 -9"	5'-712"	2.8	111	3000	418	2.00	8.370	6,500	
		750HA	3 -150= Fig-	911.	5'-11'2"	2.9	135	3200	520	2.48	10.4	75014	
1			3'-150= Fig-	7 -0"	5'-312"	2 -10	163	3400	622	294	12.45	A DISTUIR	
1			3"-150= Fig	7.0"	6.712"	2 -11"		4000	732	3.48	14.64	Inc ma	
			3"-150= Flo	7'-0"	6-11	30		4600	847	4.05	16.95	i i i i i i i i	-
		AHUUCI	3"-150= Fig:	7'-0"	7-312"	31.	257	5400	1037	4.66	20.74	1500HA	

tFlg = 150# A.S.A. R.F. Flange (A.S.A. B 16.5)

#### DEFINITIONS as defined in NEMA Standard AD-1-1959

CYCLE is the time allowed for a desiccant bed to be in dr/ing service, reactivated, and returned to drying service.

STANDARD CUBIC FEET PER MINUTE (SCFM) is the flow rate which, for convenience, has been referred to standard conditions of 70°F and at an atmospheric pressure of 29.92 inches as measured on a mercury barometer.

NEAT-LES FORMULAE

3. 
$$V_3 = \frac{1.1 \, V_1}{P_T}$$

$$\int_{1.} T = \frac{30 \, \text{CPr}}{V_1}$$

2. 
$$L = \frac{2C(Pr-1)}{T}$$

V<sub>1</sub> = inlet volume of air or gas being dried (SCFM) = net output of dry air (SCFM)

= purge rate (SCFM)

T = cycle time (minutes)

P = inlet pressure (PSIG)

 $Pr = pressure ratio = \frac{P + 14.7}{14.7}$ 

U == chamber velocity (ft. per minute)

A = chamber area (sq. ft.) See specification table

C = chamber volume (cu. ft.) Sec specification table

L = air discharged to atmosphere each time chamber is dumped (SCFM) (based upon empty chamber)

IMPORTANT - chamber velocity (U) must not (use next size dryer if neces

Cycle "1" (minutes)	1
2	
3	
1	

Note #1: formula #1 may be used to cold cycle time permissable, when a dryer is a maximum capacity. This results in the maximum.

Note #2: When input volume is reduced."
also be reduced as calculated by formula #

e Gauges indicator

25

np)\*

= Alarm ontacts)

· Gauges indicator

### HOW TO ORDER

The accompanying information may be used in the selection of the proper Heat-Les Dryer. Your local Trinity representative is available to assist you in this. These men are trained to size and recommend the proper dryer for your requirements. They will consult with you, make recommendations, present costs, and will aid you in the installation and operation of your Trinity Heat-Les Dryer.

When ordering by standard model number, it is recommended that you include the following information:

1. Type of gas being dried.

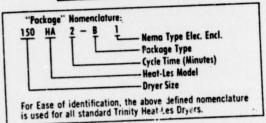
2. Inlet f.ow (SCFM)

Volume of useable dry air or gas (SCFM)

Temperature of air or gas to be dried.

5. Pressure of gas or air to be dried.

6. Operating voltage \_ \_ cycles



NOTE: The above NEMA 1 dryers can be supplied in either NEMA\*4 or NEMA\*7 electrical construction by specifying Package A4 or B4 for NEMA 4, or Package A7 or B7 for NEMA 7.

Trinity Standard Heat-Les Dryers are suitable for operating pressures from 60 psi to 150 psi at a maximum inlet temperature of sures from 60 psi to 150 psi at a maximum inlet temperature of 120°F. Higher pressure ratings are available on special order. Heat-Les dryers are normally not recommended for operating pressures below 60 psi due to relatively large purging losses. However requirements for extremely low dewpoints may still indicate the desirability of a Heat-Les dryer for these applications. It is suggested that they be referred to the factory for recommendations.

						INLET PO	ESSURE -			125 1	PSIG	150 P	SIG	SIZE
60.0	5 5	7) 73	·6	82 P	110	2 PJ		100 1	CITLET	ITILET	OUTLET	INLET	OUTLET SCEM!	
SCHALL	0.7.57	20 UI \$4.75	9.1.1.	STA	Silviv	SET !	Quite!	SOF Y	FCEAT.	SCH	2.43	3.43	3.00	2.3
				1.93	1.50	2.13	:::	2.04	1.97	2.83	4.01	5.55	4.81	1.1
		7.3		3.15	2.53	3.5	1	3.55	3.23	€.55	5.84	2.05	€.97	
2/-	- 1		3.12	4 53		5 13			2.51	12.5	10.66	14.3	12.32	1. 1
			7:11	3.5	1.3	1.4	7	25.3	21.16	30.3	26.28	36.3	31.45	25nA
16.6	13.23	18.7	14.95	20.8	17.00	23.1	19.09	25.5	1	-				
	10.20									i	54	74	64	35HA
			30	43	35	47	38	52	43	96	81	112	96	50HA
34	. 26	38 59	47	65	53	72	59	78	65	165	140	195	167	100HA
51	39	100	80	110	89	125	102	135	112	260	220	305	262	150HA
88.5	108	160	128	175	142	195	160	215	253	370	313	440	378	200HA
139	156	230	183	255	206	280	230	305	255	"				
									1	455	385	535	458	300HA
	1	2:5	226	310	250	340	278	375	310	605	511	710	809	407HA
253	1 193	200	014	41.	3.53	450	353 _	1 495	410	770	570	905	751	1 1 1
311		1-273-	531	521	4	575	9	630	641	950	205	1130	952	10
				11637	522	720	2.2	7:0	753	1105	975	1000	1174	1
			E72	7:3		3.5	/10	1160	552	140	1171	165 ;	1402	1 1 A
		****				11	1 501	1360	1115	11500	1302	19.7)	1658	1 "
						1740		1580	1298	1920	1610	2270	1931	
							* * * * * * * * * * * * * * * * * * * *	1 15	12.55	1 1323	1842	1 2620	2216	1 16 1

\*The above outlet flows reflect all losses (i.e. Purge and chamber dump)

1) must not exceed 50 ft./min. er if necessary)

Factor "K"	
 0.75	
 0.833	
 0.875	

sed to calculate the maximum 2 dryer is not operating at its in the minimum chamber loss

s reduced, the purge rate may tormula #3

Note #3: When dewpoint requirements are not severe, the purge Note #3 when dewpoint requirements are not severe, the purge rate may frequently be reduced below the calculated figure. This reduction should be done gradually (with frequent dewpoint checks) so that the stabilized conditions are reflected in the results.

EXAMPLE: Problem: Select proper dryer and determine dry air output if: Inlet flow = 190 SCFM Inlet pressure = 125 PSIG NEMA 4 electrical enclosure, "A" type package

Solution:

1. From capacity chart it will be noted that a dryer size 150 HA is required.

2. Determine cycle time:

$$T = \frac{30 \times 2.084 \times 9.5}{190} = 3.1 \text{ minutes (max. time cycle)}$$

(Note: available standard cycles are 2, 3, or 4 minutes) Therefore, select 3 min. cycle

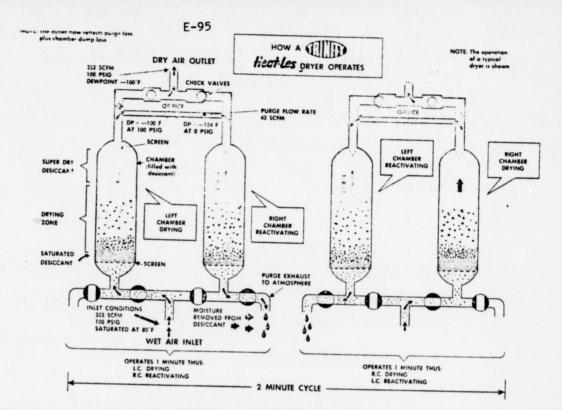
3. Determine dry air output:

Determine dry air output:  
Purge rate: 
$$V_3 = \frac{1.1 \times 190}{9.5} = 22 \text{ SCFM}$$
  
Chamber dump:  $L = \frac{2 \times 2.084 (9.5-1)}{3} = 11.8 \text{ SCFM}$ 

Dry air output:

V2 = 190-11.8-0.833 x 22 = 160 SCFM The required dryer package would be: 150 HA3-A4

FILTERS: It is normally recommended that a suitable prefilter be installed ahead of each dryer to assure the most efficient operation. Also, when the useage so dictates, an appropriate after should be used after the dryer. Trinity offers a complete line of filters. line of filters.



# ... HOW IT OPERATES

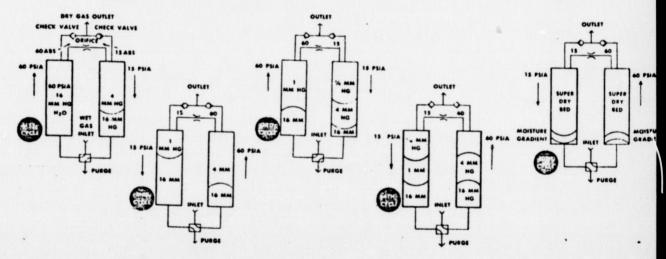
### THEORY OF OPERATION

Heat-Les Dryers utilize the natural tendency of desiccants to come into equilibrium with their surroundings. During the drying cycle, the desiccant adsorbs moisture from the incoming gas stream. During the reactivation cycle, a small portion of the super-dry gas is passed over the desiccant at atmospheric pressure, creating an environment in which the desiccant must give up the previously adsorbed moisture to reach equilibrium.

#### **ACTUAL OPERATION**

As shown in the above flow diagrams, the Heat-Les Dryer cycles between two desiccant chambers, one serving as a drying medium, while the other is undergoing a reactivation process. The diagram at left shows the wet gas entering at the bottom of the left-hand chamber, passing upward through the desiccant where it is dried to an extremely low dewpoint. The dry air passes through the check valve to the dry air outlet. Simultaneously, a small percentage of the dry gas is expanded through the orifice between the chambers, and flows down through the right-hand chamber, reactivating the desiccant, and passing out through the purge exhaust. At the end of the cycle, the chambers are automatically reversed, the right-hand chamber serving as the drying medium, while the left-hand chamber is being reactivated, as shown in the diagram at right.

The following diagrams illustrate how the reactivation of a Heat-Les dryer progresses from initially saturated beds (represented by 16 mm vapor pressure) to the conditions represented by the final illustration, wherein the major portion of each bed is super-dry and thus capable of producing super-dry gas.

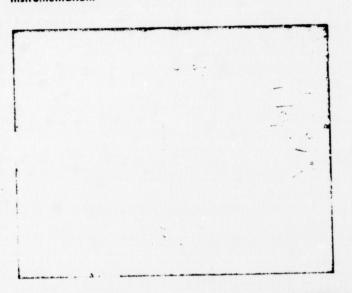


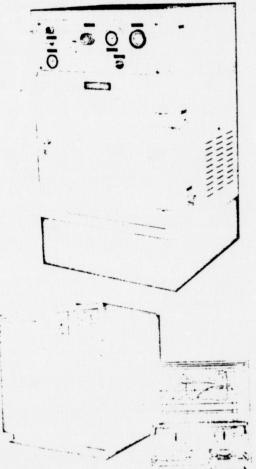


# **UNITIZED DRY-AIR SYSTEMS**

# Incorporating the Cartles DRYER

Trinity also designs and manufactures complete, Unitized Dry Air Systems for the commercial and military user in a wide range of capacities and pressures. The heart of these systems is a Trinity Heat-Les Dryer, thus offering the user all the inherent advantages of the Heat-Les design, including very low dewpoints, minimum operating costs, and low initial costs. These systems are offered to users who do not have existing or sufficient air supplies. Trinity Unitized Dry Air Systems are completely assembled, ready-to-operate systems with matched components consisting of compressor, accumulator, Heat-Les Dryer, filters, controls, and instrumentation.





### OTHER



## **PRODUCTS**

#### Type A Dryers

Atmospheric regeneration type dryers employing electric or steam heat reactivation. See Bulletin A-309

#### Type AB Dryers

Atmospheric blower type dryers employing electric or steam heat reactivation. See Bulletin AB 310

#### Thermowells

Protective wells for heatsensing instruments including thermocouples, filled systems, bi-metallic thermometer's and test instruments. See Bulletins TT-301, TT-302, TT-303, TT-305, TT-304, TT-307

#### Filters

A complete line of mechanical filters and oil vapor adsorbers. See Bulletins FP-311, FA-312, FM-313, FC-314, FD-315, FK-316.

#### Thermocouples

All types of thermocouples and thermocouple assemblies including miniaturized selfsheathed. See Bulletins TT-306, TT-317

THE TY ROUPS THAT CORPORATION,

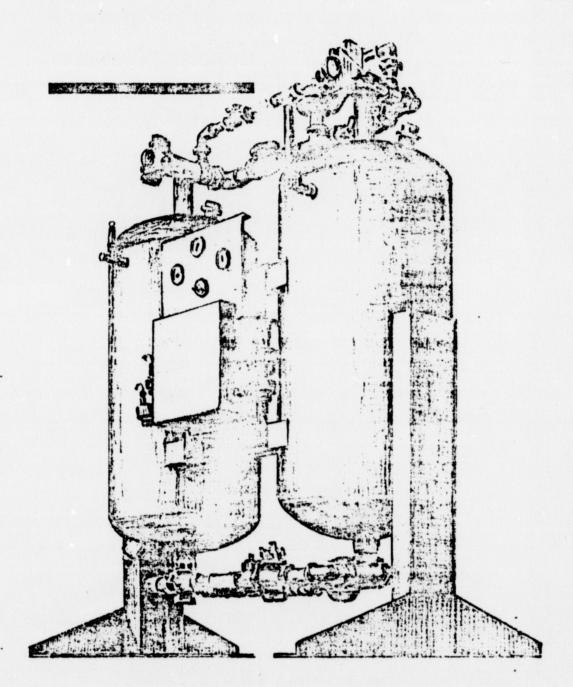
PLAINTIFF'S EXHIBIT 6D

Pall Trinity Micro Corporation Bulletin HA-308C









# PALL TRINITY MICRO CORPORATION



A SUBSIDIARY OF PALL CORPORATION

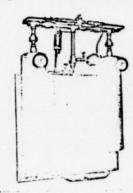
CORTLAND, NEW YORK 13046, U.S.A. . (607) SK 6-7535 . TWX 607-371-1266 . CABLE: TRINCORT

# TYPE HA Heat-les' DRYERS

#### **FEATURES**

- Provides super-dry air or gas with dewpoints as low as --100°F at line pressure.
- Eliminates . . . the need for costly heaters with controls . . . avoids subsequent burnouts and leakage.
- Negligible increase in temperature of effluent gas.
- Corrosion reduced due to low temperature operation and reactivation.
- Adjustable purge rate...reduces gas consumption when dryer is not being operated at full rated capacity.
- Desiccant capacity maintained...moisture is removed from desiccant by counter-current low temperature dry purge gas avoiding desiccant degradation caused by high temperature reactivation. Low temperature reactivation prevents the formation of oil varnish coatings on desiccant beads...thus maintaining desiccant adsorptive efficiency.
- Repressurizing feature. Chamber pressure equalized before switchover to prevent desiccant breakup and downstream line surges.
- Fail-safe design. Both chambers automatically adjust and continue to deliver low dewpoint air or gas long after electric power failure.
- A stainless steel support is provided in each chamber to retain the desiccant and diffuse the inlet flow for maximum bed utilization.
- Separate desiccant drain and fill ports are provided as standard equipment on models 51 and larger. This:
  - a) eliminates the need to disconnect piping when recharging the dryer.
  - b) automatically limits the bed height to guarantee the plenum area necessary for a uniform inlet flow profile thru the desiccant bed, and assuring proper dispersion of the purge gas.
- Equipped with 40 micron stainless steel pilot air filters . . . assures trouble-free, automatic operation by protecting control valves.
- Ideally suited for intermittent duty since extended reactivation period is not required.
- Dewpoint and capacity not affected by wide fluctuations in inlet temperature.
- Models 301 and larger include cleanable stainless steel outlet filters on each chamber preventing desiccant bead carryover. Filters may be removed for cleaning without disturbing the desiccant bed.
- All desiccant chambers are ASME designed. Models 51 and targer are U stamped or UM stamped in accordance with the requirements of the UPV code.
- Lower initial, installation, operating and maintenance costs.

The **original** Heat-Les dryer using adsorbents to produce super-dry gases or air. Dewpoints of  $-40^\circ$  are easily obtained as well as dewpoints of  $-100^\circ$ F or lower . . . far below those available with other designs. Reganeration of the desiccant is automatic . . . no heaters are involved. Drying is continuous in the up-flow direction with down-flow purge exhausting to atmosphere. The **PTM** Heat-Les dryer assures dependable and **ECONOMICAL** operation.



# Type HA Models 2 to 25 Wall Mounted Dryers

For drying small flows from 1.5 SCFM of compressed air or gases at up to 150 PSI. Higher pressure units available. Standard units provided with chamber pressure gages.

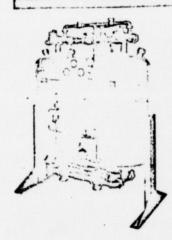
Unit shown, Model 25HA-1-0000F0



#### Type HA Models 35 to 201 Floor Mounted Dryers

Designed to dry intermediate volumes from 34 SCFM of compressed air or gas at up to 150 PSI. Higher pressure units available. Standard units provided with exhaust muffler, relief vaives and locally mounted chamber pressure gages and purge flow indicator.

Unit shown, Model 151HA-4-0000CS



#### Type HA Models 301 to 3001 Floor Mounted Dryers

Designed to handle flows from 255 SCFM and up. Units available for pressures up to and including 10,000 PSI. Standard units provided with exhaust muffler, relief valves, and locally mounted chamber pressure gages and purge flow indicator.

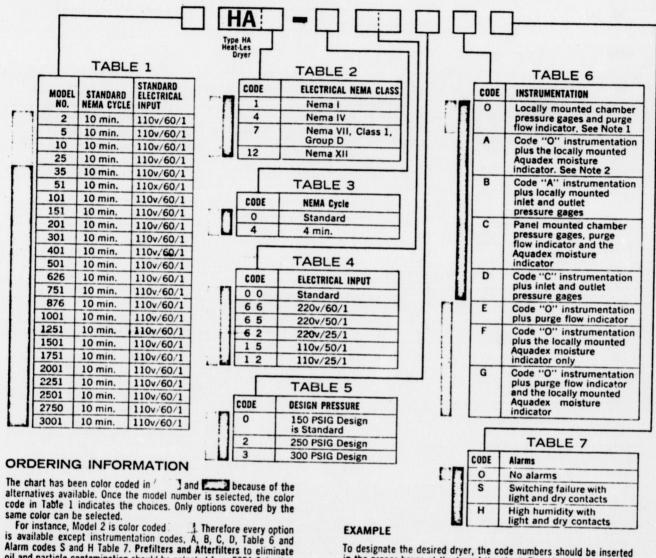
Unit shown, Model 401HA-1000CS

# REFERENCE CHART

DESIGN FLEXIBILITY—The chart below provides data on standard models as well as options which can be selected for each model. Once the proper size unit is selected from Table 1 (based on operating conditions) various options can be included to meet your particular requirements. By selecting Electrical Nema Class. Nema Cycle, Electrical Input, Design Pressure, Instrumentation, and Alarms, specified design can be obtained. An illustration of the procedure is shown below.

To assure fast deliveries, all standard units are pre-engineered production models; with the more popular ones carried in stock. Optional parts are also warehoused at the factory, assuring quick delivery when optional features are added to standard models. All units are pre-tested at the factory and quality controlled prior to shipment. Dryers are shipped pre-charged with desicant so they are ready to operate after simple installation.

Our reputation for producing the finest adsorptive dryers available is based on an engineering approach to design and manufacture. A world wide network of PTM trained field representatives and a staff of factory engineers are on call to be of assistance in solving unusual dryer problems.



### Guide, pages 5, 6, 8 and 15.

 Models 2 through 25 include chamber pressure gauges but do not include "Purge Flow Indicator" as standard. See Options E, F, G.
 AQUADEX\* moisture indicator provides a constant visual check of satisfactory dewpoints and satisfactory mechanical operation of the dryer. Desiccant can be changed very easily without shutting down operation or disassembling the unit from mounting. See bulletin MI-321.

oil and particle contamination should be selected from E25A Selection

EXAMPLE

To designate the desired dryer, the code numbers should be inserted in the proper boxes at the top of the chart. Therefore:

> Table 2 Table 3 Table 4 Table 5 Table 6 Table 7 151 HA:1 - 0 0:0 0 A

would be a Model 151 unit, Heat-Les dryer with NEMA I electricals. Standard NEMA cycle of 10 minutes. Standard Electrical input of 110 volts/60/1, 150 psig design, Instrumentation is: locally mounted chamber pressure gages, purge flow indicator, and the locally mounted Aquadex moisture indicator, no alarms.

All zeros following last option can be omitted.

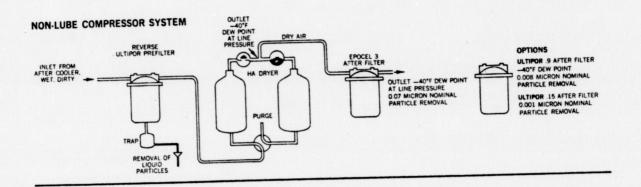
T.M. PALL CORPORATION

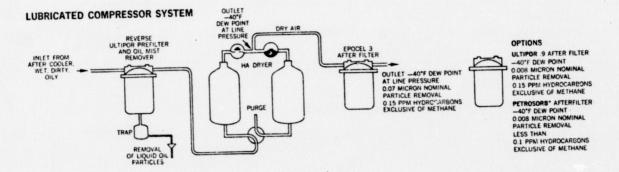
# OIL CONTAMINATION AND FILTRATION

A pre-filter and an after-filter should be included with all dryer installations. Desiccants should be protected from contaminants such as oil, pipe scale, liquid water, foreign liquids and dirt. Although PTM Heat-Les Dryers have a tendency to reject oil entering with the incoming gas, complete oil elimination is not positive and may appear in the effluent. Oil in varior form will be rejected by the dryer but oil mist will settle on the desiccant causing its degradation and will be swept on downstream.

PTM manufactures a complete line of fine filtration equipment as well as all types of dryers. A result of this experience is development of an exclusive pre-filter known as the RE-

VERSE ULTIPOR\* filter which not only will remove 99% of all incident liquid-oil but will also provide 98% removal of all solid contaminants larger than 0.04 microns! This represents a level of purity heretofore unavailable without using more costly equipment. This equipment permits reliable, low cost oil-lubricated compressors to be used for most applications that have previously been restricted to the oil-less type. **PTM** has also developed special after-filters known as the Epocel filter or the standard Ultipor filter. Levels of purity obtained are shown in the flow diagrams. A combination activated carbon-Ultipor filter known as the Petrosorb\* filter can be installed downstream of the dryer as an alternate providing quantitative removal of hydrocarbons exclusive of methane.





#### DIMENSIONS

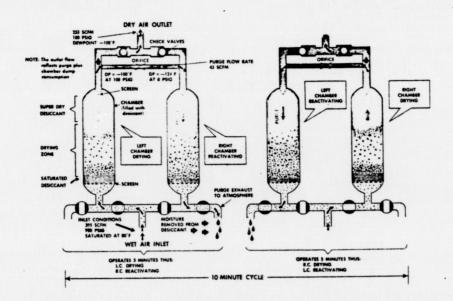
Dryer Size	Size Connections	Height	Width	Depth	Weight (1bs)
2 HA	1/4" NPT	24½"	16¼"	7"	40
5 HA	1/4" NPT	24½"	18¼"	5½"	45
10 HA	1/4" NPT	24½"	19¼"	5½"	49
25 HA	1/2" NPT	34"	24"	9½"	115
35 HA	3/4" NPT	57'%"	291/4"	21¾"	260
51 HA	1" NPT	52%"	293/4"	19¾"	370
101 HA	1" NPT	68%"	29¾"	19¾"	440
151 HA	1½" NPT	60%"	37½"	23"	500
201 HA	1½" NPT	71%"	37½"	23"	620
301 HA	2"-150# FLG.	67%"	51"	27"	960
401 HA	2"-150# FLG.	67%"	51"	27"	1.140
501 HA	2"-150# FLG.	771/4"	51"	27"	1.320

Dryer Size	Size Connections	Height	Width	Depth	Weight (lbs)
626 HA	3"-150#FLG.	75¼"	66 %"	33"	2,200
751 HA	3"-150#FLG.	83¼"	66 %"	33"	2,530
876 HA	3"-150#FLG.	91¼"	66 %"	33"	2,840
1001 HA	3"-150# FLG.	90"	71"	38"	3,900
1251 HA	3"-150# FLG.	94"	71"	38"	4,870
1501 HA	3"-150# FLG.	100"	71"	38"	5,800
1751 HA	4"-150# FLG.	104"	76"	42"	6,600
2001 HA	4"-150# FLG.	1061/4"	80"	42"	7,350
2251 HA	4"-150# FLG.	1115/4"	84"	46"	8,050
2501 HA	4"-150# FLG.	120"	98"	48"	8,800
2751 HA	4"-150# FLG.	120"	104"	48"	9,400
3001 HA	4"-150# FLG.	120"	108"	49"	10,000

# HIGHEST PERFORMANCE AT LOWEST INITIAL, INSTALLATION AND OPERATING COSTS

**PTM** HEAT-LES DRYERS have dramatically expanded the use of desiccant dryers for many industrial requirements. Drying without heat, by means of a unique method of regeneration, has created wide demand for **PTM** Heat-Les units in drying instrument air, process gases, blanket gas, communications system purging and many other applications.

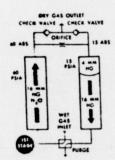
Having pioneered the development of this system in 1957, PTM Corporation (formerly Trinity Equipment Corporation) has placed over 3,000 Heat-Les Dryers in service throughout the world. A planned program of research engineering, steadily improving the original designs, has made the PTM Heat-Les Dryer an industry standard for performance and economy.

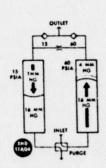


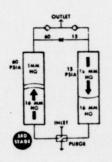
THEORY OF OPERATION—Heat-Les Dryers utilize the natural tendency of desiccants to come into equilibrium with their surroundings. During the drying cycle, the desiccant adsorbs moisture from the incoming gas stream. During the reactivation cycle, a small portion of the super-dry gas is passed over the desiccant at atmospheric pressure, creating an environment in which the desiccant must give up the previously adsorbed moisture to reach equilibrium.

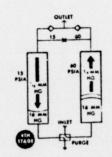
ACTUAL OPERATION—As shown in the above flow diagrams, the Heat-Les Dryer cycles between two desiccant chambers, one serving as a drying medium, while the other is undergoing a reactivation process. The diagram at left shows the wet gas entering at the bottom of the left-hand chamber, passing upward through the desiccant where it is dried to an extremely low dewpoint. The dry air passes through the check valve to the dry air outlet. Simultaneously, a small percentage of the dry gas is expanded through the orifice between the chambers, and flows down through the right-hand chamber, reactivating the desiccant, and passing out through the purge exhaust. At the end of the cycle, the chambers are automatically reversed, the right-hand chamber serving as the drying medium, while the left-hand chamber is being reactivated, as shown in the diagram at right.

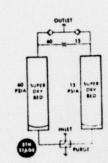
The following diagrams illustrate how the reactivation of a Heat-Les Dryer progresses from initially saturated beds (represented by 16 mm vapor pressure) to the conditions represented by the final illustration, wherein the major portion of each bed is super-dry and thus capable of producing super-dry gas.

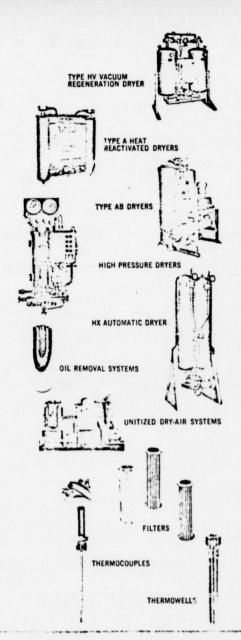












# OTHER PALL TRINITY MICRO ENGINEERED EQUIPMENT

FOR THE CONTROL OF FLUIDS AND ENVIRONMENTS.

TYPE HV Heat-Les VACUUM REGENERATION DRYER to reduce purge air requirements. TYPE A DRYERS Atmospheric regeneration type dryers employing electric or steam heat reactivation. TYPE AB DRYERS Blower-type dryer with no purge consumption for use in large flow or critical gas applications and with highly fluctuating flows. HIGH PRESSURE DRYERS PTM has designed and built many Heat-Les and Heat-Regenerated high pressure dryers for gases to 8000 SCFM and 10,000 PSIG for specific military and commercial applications. Special dryers for liquid drying, gas purification and separation can also be furnished. HX AUTOMATIC DRYER Superior to previously available dryers because of higher thermodynamic efficiency resulting from exclusively designed heat transfer members. Contains the DRYATROL Control, which is a self-contained valvetimer module, pneumatically controlled, performing all timing and airflow functions, ideal for remote or hazardous locations since no electrical connections are required. Unit is explosion-proof. OIL REMOVAL SYSTEMS Full line of filtration equipment which when used with PTM Dryers can produce effluents of less than 0.1 ppm hydrocarbons, exclusive of methane. Submicron removal ratings are achieved. UNITIZED DRY-AIR SYSTEMS Completely packaged, readyto-operate systems including compressor, dryer, accumulator, and instrumentation. FILTERS PTM offers the widest range of cartridges and assemblies for every filtration requirement. THERMOWELLS Protective wells for heat-sensing instruments including thermocouples, filled systems, bi-metallic thermometers and test instruments. THERMOCOUPLES All types of thermocouples and thermocouple assemblies including miniaturized self-sheathed.

SALES AGENTS Albuquerque Atlanta Baltimore Baton Rouge Birmingham Boston Buffalo Butte

Charleston

Charlotte

Chicago Cincinnati Cleveland Davenport Denver Petroit LI Paso Fort Lauderdale Hamden Houston Indianapolis Kansas City Kingsport Knoxville Los Angeles Milwaukee Minneapolis Mobile New York Omaha Paducah Philadelphia Phoenix Pittsburgh Portland Richmond San Francisco Seattle St. Louis

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M. PALL CORPORATION



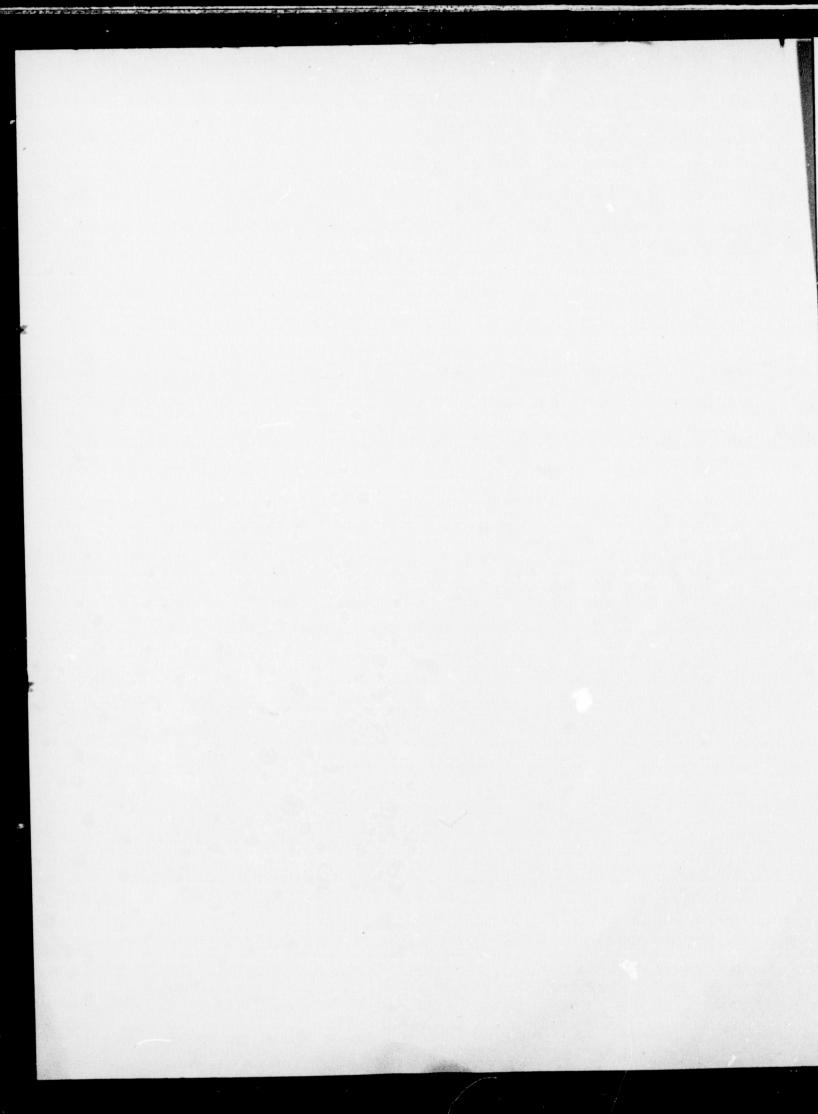
# PALL TRINITY MICRO CORPORATION

A SUBSIDIARY OF PALL CORPORATION

CORTLAND, NEW YORK 13046, U.S.A. . (607) SK 6-7535 . TWX 607-371-1266 . CABLE: TRINCORT

# PLAINTIFF'S EXHIBIT 9

Those portions of Kahn Affidavit, filed June 27, 1968, designated Exhibit 120 and Exhibit 121.



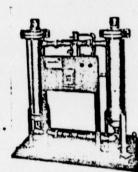


### KAHN HEATLESS DESICCANT AIR DRYERS

#### Reactivated without heat

Check these advantages:

- \* Costs reduced on installation and maintenance.
- \* Steam and electric heaters eliminated . . . reducing utility costs.
- \* Constant outlet gas temperatures.
- \* Explosion proofing eliminated.



It's

#### KAHN DRYERS

all the way . . .

Kahn has a complete line of electric or steam regeneration dryers—automatic, semi-automatic or manual operative. Operating pressures up to 5,000 psi.

Write for complete information.



MARTFORD 1, COMM.

This Kahn advertisement appears in the November 1957 issues of Chemical Engineering Progress and Instruments and Automation; also scheduled to appear in the above publications and Compressed Air,

January through October, 1958

### MATERA FICE CORRESPONDENCE

KAHN & COMPANY, INC.

HARTFORD 1, CONN.

ALL REDF ESENTATIVES

Dave November 11, 1957

SAL W NDBUR STREET

HEATERLESS DEHYDRATION

Whit the accordising in "Chemical Degineoring" and Instruments and Amenation" breaking, you will be asked questions about our heaverless to ydrafters.

As this point, the following information, while admittedly manger, should not prou-

Memberious ichydraffon is primarily advantageous in tigh presente applications, 1506 par and up. At this point we do not believe it practices on how presente instrument sir. This dryer is based on the principle that resist desicents tonds to give up its modestere to a stream of dry air, with which it is purged. The percentage of dry air requires for purging decreases your rapidly as an expensive greatery increases. Theoretically, approximately 15% of the increasing air apolic be required for purging at 100 psi; while at 5000 psi, loss than a fraction of 1% is meeded.

In the converte tal reactivation system, the moisture is driven out by heat plus purge. In the high pressure, for reasons given above, we found it not only practical, but very efficient, to eliminate the heat with the rather original system we devised.

The theoretical concepts involved are quite complex and need not be gone into by you with the prospect, who, after all, is interested in results only.

The adventages are startling on no beaters, no explosion barard, extremely simple muchanism, reduced cost.

The advertisements should give you numerous inquiries; in all cases, got a questionaire completed, as we would not want to have a hospitess unit applied where it is out of order.

Vory truly yours, KAHN AND COMPANY, INC.

mc/st

Irving L Kain Prosident

#### INTER-OFFICE CORRESPONDENCE

ELECTRONIC EQUIPMENT	541 Windsor Street Hartford 1, Conn PHONE CHapel 6-7431
TOALL REPRESENTATIVES	DATE November 11, 1957
ATTENTION OF	REF. YOURS
SUBJECT HEATERLESS DEHYDRATION	

With the advertising in "Chemical Engineering" and "Instruments and Automation" breaking, you will be asked questions about our heaterless dehydration.

At this point, the following information, while admittedly meager, should help you.

Heaterless dehydration is primarily advantageous in high pressure applications, 1500 psi and up. At this point we do not believe it practical on low pressure instrument air. This dryer is based on the principle that moist desiccant tends to give up its moisture to a stream of dry air, with which it is purged. The percentage of dry air required for purging decreases very rapidly as the operating pressure increases. Theoretically, approximately 15% of the incoming air would be required for purging at 100 psi; while at 5000 psi, less than a fraction of 1% is needed.

In the conventional reactivation system, the mositure is driven out by heat pins purge. In the high pressure, for reasons given above, we found it not only practical, but very efficient, to eliminate the heat with the rather original system we devised.

The theoretical concepts involved are quite complex and need not be gone into by you with the prospect, who, after all, is interested in results only.

The advantages are startling -- no heaters, no explosion hazard, extremely simple mechanism, reduced cost.

The advertisements should give you numerous inquiries; in all cases, get a questionnaire completed, as we would not want to have a heaterless unit applied where it is out of order.

Very truly yours,

KAHN AND COMPANY, INC.

ILK/tj

Irving L. Kahn President Plaintiff's Answers to Defendants' First Set of Interrogatories, pp. 9, 15-17

Answer	10.:
MINDING	

Country	Ser. No.	Filing Date	Pat. No.	Granted Date
Argentina	167,190	3/21/61	130,588	10/17/52
Belgium	471,014	7/11/60	592,854	7/29/60
Canada	753,688	6/20/58	647,868	9/4/62
Colombia	71,937	4/20/61	10,771	12/28/61
France	769,637	7/4/58	1,207,699	9/7/59
Germany	E16071	6/30/58		Pending
Gr. Britain		6/20/58	850,443	1/25/61
Greece	. 26,902	4/10/63	26,595	9/1/64
Japan	18852/58	7/5/58		On appeal from opposition
Japan	35528/60	8/15/60	318,101	3/15/66
Libya	812/212	11/23/61		Pending
Malaya	6/1962	1/17/62	6/1962	1/23/62
Netherlands	229,316	7/4/58	112,691	3/16/66
Spain	265,446	3/7/61	265,446	6/17/61
Switzerland	61,394	7/4/58	409,875	3/31/66
Venezuela		3/17/61	13,555	10/17/63
				+ 0001 in 011

No art was cited by the Patent Offices in all

countries where this case was filed with the following exceptions:

Germany:	German Patents	520,709 546,138 846,095 871,886 882,541 891,837 970,223
•	Swiss Patent	212,189
	"Brennstoff- Chemie"	1954, p. 329
Gr. Britain:	British	677,150
Netherlands:	German British German U.S. German U.S.	970,223 582,045 882,541 2,747,681 871,886 2,699,837
"Chemie Ing	Technik", Vol. 144-1 (1954	25 (1953) pp. 48 and Vol. 26

the date of termination, if any, and the person signing the license and the licensee, together with the attorneys that handled the license for plaintiff.

AEI-Birlec Limited
33, Grosvenor Place
London, S.W. 1, England
Date of License: July 1, 1964
P. F. Hancock
Esso - J. K. Small

Applied Pneumatics, Inc.
740 Colfax Avenue
Kenilworth, New Jersey
Date of License: July 12, 1960
Terminated and replaced by agreement
dated August 24, 1961. Latter license
in turn terminated April 16, 1962.
Robert C. Axt, President
Esso - P. H. Smolka

Deltech Engineering, Inc. 1226 Dargue Road New Castle, Delaware Date of License: February 1, 1967 H. O. Neukomm, President Esso - R. I. Pearlman

Dielectric Products Engineering Company, Inc. Raymond, Main
Date of License: January 15, 1962
Joseph Kinney, Jr., Vice President
Esso - R. D. Manahan

Droogtechniek + Luchtbehandeling N.V.
Nieuw Mathenesserstraat 39
P.O. Box 6047
Rotterdam 7
The Netherlands
Date of License: October 1, 1967
Ir P.G. Cazemier, Joint Managing Director
Esso - R. I. Pearlman

Dryvent Limited
Hollygrove House
Staines Road, Hounslow
Middlesex, England
Date of License: September 1, 1954
C. Potts, Managing Director
Esso - R. I. Pearlman

Gas Atmospheres, Inc. 5353 West 161st Street Cleveland, Ohio 44142 Date of License: January 1, 1967 W. H. Boyd, President Esso - R. I. Pearlman Ges Drying, Inc.
Box 56
Summit, New Jersey
Date of License: June 1, 1959
Date of Termination: January 1, 1967
Dayrel G. Hoke, Vice President
Esso - L. A. Strimbeck

General Metals Corporation 4223 Monticello Boulevard Cleveland, Ohio 44121 Date of License: January 1, 1966 R. A. Swanson, Vice President Esso - R. I. Pearlman

Gilbert & Barker Manufacturing Company West Springfield, Massachusetts Date of License: April 1, 1962 Irving C. Jacobs, President Esso - R. D. Manahan

Cie Gohin-Poulenc
11/13 av. A. Netter
Paris 12°, France
Date of License: January 1, 1959
M. P. Baduel d'Oustrac, Directeur General
Esso - R. I. Pearlman; L. A. Strimbeck; J. K. Small

McGraw-Edison Company
P. O. Box 2077
Milwaukee 1, Wisconsin
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Puregas Equipment Corp. 1445 Strongs Road Copiague, New York 11726 Date of License: July 1, 1965 John P. Adams, Vice President Esso - R. I. Pearlman Rimer Manufacturing Company Limited
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Great Britain
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Date of License: April 25, 1962
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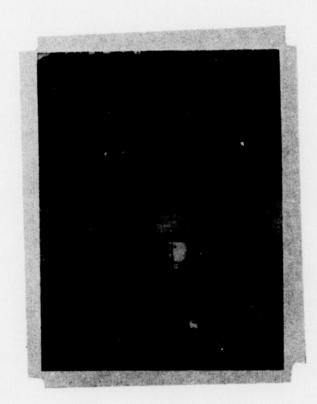
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Lockport, New York
Date of License: November 1, 1964
James R. Meyer, President
Esso - R. I. Pearlman

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Cortland, New York
(Bought up original Trinity Equipment Corp.)
Date of License: March 1, 1958
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PLAINTIFF'S EXHIBIT 15A

Photograph of Heaterless Dryer



### PLAINTIFF'S EXHIBIT 16

General Description of the Skarstrom Heaterless Dryer Invention

#### General Description of the Skarstrom Heaterless Dryer Invention

A completely self-contained, self-regenerating gaseous fractionating process utilizing a selective adsorbent in which the adsorbent bed is the sole agent for fractionation and heat exchange which comprises:

- (1) a repetitive adsorption/desorption process utilizing differences in pressure;
- (2) wherein gaseous feed is introduced at one end of the adsorbent bed and product effluent recovered at the other end;
- (3) a part of the product effluent is used to desorb the bed (or essentially the same product effluent from a paired companion bed on a complimentary cycle);
- (4) by counter-current flow at lower pressure than the adsorption pressure;
- (5) with cycle times sufficiently short so that heats of adsorption/desorption are substantially retained and balanced within the adsorbent bed;
- (6) the adsorption/desorption being effected so as to create an oscillating concentration front which remains in the adsorbent bed with only a fraction of the adsorbent bed being utilized for most of the adsorption/desorption;
- (7) said process operating so as to eliminate the need for any supplemental heat exchanges, and
- (8) the need for any external purge gas supply.

Cover Page and Pages 458-59 of German Text

"Patentgesetz Gebrauchsmustergesetz"

C.H. Beck'sche Verlagsbuchhandlung

Munchen 1973

# Patentgesetz Gebrauchsmustergesetz

mit den erganzenden Vorschriften

Kurzkommentar

begründet von

Dr. Georg Benkard

welland Rechtsanwalt beim Reichsgericht, suletzt Bundesrichter beim Bundesgerichtshol

#### fortgeführt von

Dr. Hans Bock Bundesrichter a. D.

Werner Ballhaus Richter am Bundesgerichtshof

Dr. Karl Bruchbausen Richter am Bundesgerichtshof Richter am Landgericht

Rüdiger Rogge

6., neubearbeitete und erweiterte Auflage

(Zitierweise: Benkard)

C.H. BECK'SCHE VERLAGSBUCHHANDLUNG MÜNCHEN 1973



dungen ohne weiteres auf eine besondere Art der Anordnung eines Mittels hinlenken, RG GRUR 38, 865, 867. Bedeutet die Wirkung eines Merkmals für den Fachmann nichts Ungewöhnliches, so bedarf es darüber keiner besonderen Angabe in der Patentschrift, RG GRUR 38, 865, 867. Läßt die Anspruchsfassung zwangsläufig eine Vielzahl konstruktiver Gestaltungsmöglichkeiten zu, so sind diese in den Gegenstand des Patents einbezogen, BGH GRUR 64, 669, 672. Ergeben sich die weiteren Einzelheiten für den Fachmann beispielsweise schon aus dem Gattungsbegriff, der Beschreibung oder dem allgemeinen Fachwissen, so braucht der Patentanspruch im kennzeichnenden Teil nur die erfindungswesentlichen Merkmale der Lehre anzugeben, BGH GRUR 66, 201, 205 r. Sp., selbst wenn im Einzelfall durea einen zumutbaren Umfang nicht überschreitende Versuche zu ermitteln ist, mit welchen Größen der einzelnen Bauteile eine für den speziellen Fall geeignete Vorrichtung zu gestalten ist, BGH GRU3 67, 56, 58; 68, 311, 313; BGH Mitt. 72, 135, 136; BGH Ia ZR 10) 64 v. 22. 12. 1966, oder welche Arbeitsmethoden optimale Bedingungen ergeben oder ungeeignet sind, BGH GRUR 66, 312, 317 m. w. N.: vgl. auch: RG MuW 29, 499, 500; RG GRUR 38, 256, 261; 38, 424, 425. Da der Anspruch nur den wesentlichen Kern der Erfundung herausschälen soll, ohne daß eine erschöpfende Aufzählung und genaue Beschreibung aller Lösungsmittel im Anspruch notwendig wäre, BGH Liedl 63/64, 157, 168, kann der Anspruch durch der Beschreibung unschwer zu entnehmende Erganzungen klargestellt werden, BGH GRUR 62, 80, 81, ebenso durch Merkmale, die der Pachmann aus der sinngemäß verstandenen Gesamtheit der Patentschrift heraus zwar stillschweigend, aber notwendig und unzweideutig mitgesetn: fundet, RG GRUR 44, 72, 74; BGH X ZR 18 3 vom 29. 6. 1971. Aus der Beschreibung kann die nähere Kennzeichnung gewisser Merkmale im Sinne des Anspruches entnommes werden, RG GRUR 35, 913, 914 r. Sp.; 36, 480, 481; BGH GRUR 54, 107, 111; 54, 317, 319; 55, 29, 32, denn bei der Auslegung eines Patents sind die Ansprüche zusammen mit der Beschreibung 2. Ganzes zu beachten, BGH Beschl. vom 29. 1. 1970 - X ZB 2 us. Für die Patentlehre unwesentliche Zufälligkeiten, die sich in den Abbildungen der Patentzeichnung befinden und von dort auf die Wettfassung der Beschreibung und der Ansprüche zurückgewirkt hann können bei der Bestimmung des Gegenstandes des Patents auch Betracht bleiben, BGH GRUR 61, 409, 411. Ein Patent gewährt aber keinen Schutz für vom Anspruch nicht erfaßte Ausführungserspiele, BGH GRUR 66, 192, 196.

a) Die Fassung des Patentanspruchs, der in der Regel schon außerlich in einen Oberbegriff (Gattungsbegriff) und einen Kennzeich nungsteil, der die neuen Lösungsmittel enthält, aufgebaut wird, der durch die Worte "dadurch gekennzeichnet" getrennt werden, vel

4 26 Rdn. 27-29, ist als solche für sich allein für die Ermittlung des Gegenstandes des Patents ohne Bedeutung. Für den Gegenstand eines aus mehreren Merkmalen bestehenden Patents ist es belanglos, ob ein Merkmal im Oberbegriff oder im kennzeichnenden Teil des Anspruches steht, RG GRUR 32, 415, 446; 32, 577, 579; 36, 917, 919; 40, 262, 203; 42, 63, 64f.; 42, 204, 206; 43, 28, 29; 44, 122, 123; RG MuW 25/26, 39, 40; 27/28; 571 r. Sp; 32, 145, 147; 40, 96; BGH GRUR 54, 107, 111; 62, 80, 81; 64, 196, 198; 71, 115, 117; OLG München GRUR 55, 335, 336; LG Düsseldorf GRUR 57, 599. Bei einer Kombinationserfindung kann die patentbegründende Neuerung eines Erfindungsgedankens in einem im Oberbegriff stehenden Merkmal mechen werden, BGH GRUR 62, 80, 81; RG GRUR 36, 585, 586; PA GRUR 36, 252, 253; die Unterbringung des einen oder anderen Merkmals im kennzeichnenden Teil des Patentanspruchs ist kein Beweis dafür, daß gerade hierin das Erfinderische zu erblicken ist, BGH I ZR 98/58 vom 12. 4. 1960. Zum Gegenstand des Patents gehören sowohl die Merkmale des Oberbegritis als auch die Merkmale des Kennzeichnungsteils, RG CRUR 38, 315, 316. Daß ein Merkmal einer Kombinationserfindung im Oberbegriff'steht, besagt nicht, daß es für eine Gesamtkombination ohne Bedeutung wäre, RG GRUR 33, 631, 632. Der äußere Aufbau des Anspruches ist für die Bestimmung des Schutzbereiches in der Regel nicht entscheidend, RG MuW 25/26, 39, 40; 27/28, 571 r. Sp.; RG GRUR 32, 577, 579; 38, 315, 316. Im Einzelfall kann darin jedoch ein Verzicht oder eine Beschränkung zum Ausdruck kommen, vgl. Rdn. 103.

b) Daraus, daß sich im Patentanspruch Bezugszeichen, d. h. Ziffern oder Buchstaben aus der Patentzeichnung, befinden, kann für sich allein nicht hergeleitet werden, daß nur die konkreten, im Ausführungsbeispiel beschriebenen Baumittel durch das Patent geschützt seien, BGH GRUR 63, 563, 564; RG Mitt. 42, 55; RGZ 167, 339, 345. Diese dienen der Verdeutlichung, RGZ 167, 339, 345; vgl.

Mediger Mitt. 63, 81.

5. Hat das Patent mehrere Ansprüche, so ist der erste Anspruch in der Regel der allgemeinste, der den Erfindungsgedanken in seiner Gesamttragweite erfassen soll. Er wird als Hauptanspruch bezeichnet. Die nachgeordneten Ansprüche sind entweder Unteransprüche oder Nebenansprüche. Der Hauptanspruch und die Unteransprüche sind fur die Frage, ob der in ihnen verwirklichten Kombination ein allgemeiner Erfindungsgedanke in Gestalt einer Unterkombination einseiner Merkmale aus beiden Ansprüchen zugrunde liegt, als Einheit betrachten, BGH GRUR 56, 542, 546. Nimmt ein nachgeordneker Anspruch auf den Hauptanspruch Bezug, so liegt im Zweisel ein Unteranspruch vor, RG GRUR 35, 161, 162. Die Bezugnahme auf then vorangehenden Anspruch in einem nachgeordneten Anspruch bedeutet, daß dessen Inhalt als Oberbegriff für den nachgeordneten

Encyclopedia Britannica, 1969 Edition, pp. 170-73

# **ADSORPTION**

depression has been infilled with detritus brought down from both the Alps and the Apennines, but more especially the former, partly by glacial action during the Ice Age but mainly by the violent flood streams characteristic of the tributaries of that river. The combined delta of the Po, Adige, Brenta and Piave rivers shows that this process is still continuing, for its front is advancing seaward, in places by as much as 30 ft. a year. It is only with great difficulty that the channels necessary to the continued existence of Venice as a port are kept open. To protect the Venetian lagoon, sea walls extend the Lido sand bar; in Nov. 1966 the sea, driven by high gales, breached them and Venice was flooded, while farther south incursions of the sea augmented river flood in the Po delta.

Adria (q.v.), which was a flourishing port in Roman times and up till the late 12th century, and which gave its name to the sea, is now 14 mi. inland. Beside being the shallowest of all the sections of the Mediterranean, the Adriatic is also distinguished in parts by the relative freshness of its waters. Its mean salinity is approximately  $35^{\circ}/_{00}$  near the Strait of Otranto but falls to  $15^{\circ}/_{00}$  near the head of the sea where it receives the surface flow of Alpine and Apennine streams and also submarine flows from the limestone

plateaus of Istria and Dalmatia.

Though in general the Adriatic may be said to experience a Mediterranean climate, the more continental conditions prevalent over the north Italian lowland and the Danube basin are not without their effect on its northern sections. Their low winter temperatures, for example, cause the waters of the Gulf of Venice to show uniformly low temperatures at all depths during that season while off the Dalmatian coasts the surface waters are more than F. colder than the underlying layers. When the cyclonic depressions that develop over the Po basin and Gulf of Genoa during the same season move southeastward, the whole coastal area is swept by the cold wind from the northeast (the bora) which brings some danger to small craft as well as general discomfort to the population. In southern areas, a warm damp sirocco (not to be confused with the dry dusty Saharan wind of the same name experienced on the north African coast) blows from the southeast. Surface currents move anticlockwise, entering the Adriatic on the east side of the Strait of Otranto, passing northward along the Dalmatian coast, southward along the Italian shores and leaving on the westward side of the strait. The southward movement, by carrying silt from the Po delta, has extended the lowland toward Ravenna and beyond.

There is a marked contrast between the Balkan and the Italian coasts. The former is rugged everywhere north of Albania, its main features evidently formed by submergence; the latter shows mainly emergent features, though the coastal belt shrinks to a narrow ledge in the Abruzzi. Marshes, laguons and sandspits border the shores of the Gulf of Venice and extend for some distance south of the Po delta, low marshy ground reaching as far south as Rimini though narrowing to less than a mile beyond Ravenna. In northeastern Emilia-Romagna, side tracts were reclaimed by poldering. Foothills of the Apennines lie close behind the coast through the Marche and Abruzzi e Molise but from Mt. Gargano southward these are replaced by bare limestone plateaus and hills.

There is a marked absence of natural harbours all along the Italian coast. Ancona, on a bay sheltered by a limestone promontory, is the only port for many miles along the middle section. The marsh and lagoon type of coast stretches around the Gulf of Venice almost to Trieste where begins the low limestone plateau of the Istrian peniasula. Southward from the Gulf of Kvarner the coastlands rise very steeply inland, the 1,500-ft. contour being close to the sea everywhere. As far as Dubrovnik the land is fringed with islands (e.g., Krk, Cres, Brac and Curzola) and its coastal margin interrupted by frequent inlets (T- and L-shaped gulfs), all obviously produced by the submergence of valleys between the fold ranges which are there parallel to the shore line. In Albania the coastal plain is wider and more continuous but imperfectly drained.

Penetrating northward so close to the heart of central Europe, the Adriatic has always been of importance as a trade highway. From very early times traffic has passed across it between Ealy and the Balkan lands in spite of the obvious difficulties presented

by the lack of shelter on the Italian side and the absence of good natural routes leading inland from either shore. Durres (Durazzo) was the western terminus of the great Roman and Byzantine highway from Constantinople and Salonika. Dubrovnik and Split were Roman ports on the Balkan side linking with Ancona. Ravenna and Adria on the Italian. Through routes across the Apennines were difficult but, in spite of this, the latter ports also handled trade between Rome and the eastern Mediterranean because of the difficult navigation involved in the voyage by way of the Straits of Messina.

The rise of Venice gave special importance to Adriatic routes because of its easy communication with southern Germany and northwestern Europe by the Brenner pass, as well as to Vienna and the Danube highway by the Semmering pass. Long before the opening of the Suez canal (1869) the main currents of Mediterranean trade had been diverted away from the Adriatic ports. Neither that event nor the frequent boundary changes around its northern land termini have completely robbed it of its former importance. The trade of Venice and Trieste indeed increased as a result of the opening of the Suez canal. Rijeka, Dubrovnik and Split still carry on more than purely local trade; Trieste handles a large traffic and Venice manages to maintain its position as an outlet for the Lombardy plain. Bari and Brindisi are large ports, while Ancona's trade is mainly coastal.

ADSORPTION. All solid substances are known to be capable of attracting to their surfaces molecules of gases or solutions with which they are in contact. This phenomenon is known as adsorption. The solids that are used to adsorb gases or dissolved substances are called adsorbents; the adsorbed molecules are usually referred to collectively as the adsorbate. A well-known example of an excellent adsorbent is the charcoal used in gas masks. With its area of about 125 ac per pound, it is capable of adsorbing and holding large quantities of poisons or impurities that one wishes to remove from a stream of air.

Adsorption refers to the taking up of molecules by the external surface or internal surface (walls of capillaries or crevices) of solids or by the surface of liquids. Absorption, with which it is often confused, refers, on the other hand, to processes in which a substance penetrates into the actual interior of crystals, of blocks of amorphous solids or of liquids. Sometimes the word "so, ption" is used to indicate the process of the taking up of a gas or liquid by a solid without any specification as to whether the process is one of adsorption or of absorption.

It is now generally recognized that adsorption can be either physical or chemical in nature. For convenience, these two types of adsorption will be discussed separately. Adsorption from solu-

tion is also treated separately.

Applications of Adsorption.—Traditional applications of physical adsorption include the use of charcoal for removing poison gases from the air; hydrocarbons from natural gas; and oxyzen, nitrogen or other gaseous impurities from helium during the separation and purification of the latter. Later applications were concerned with the measurement of the surface area of finely divided or porous solids and with the measurement of the pore size and pore distribution of porous solids. Also, in the analytical process known as gas chromatography (see Chromatography) physical adsorption is responsible for the separation of the various components of a gaseous mixture to produce separate and characteristic peaks on the chromatograms.

Chemical adsorption or chemisorption, as pointed out below, is of general interest mostly because of its being one of the steps in catalytic processes (see Catalysis). Typical examples of important catalytic processes include, among others, the synthesis of ammonia, the cracking of hydrocarbons to form gasoline, the synthesis of methanol, the cyclization of heptane to form toluene, the oxidition of sulfur dioxide to sulfur trioxide and the hydrogenation of oils to edible fats. Chemisorption is, however, not an unmixed blessing in catalytic reactions, since it can also slow them down.

holding poisons on the catalyst surface.

Adsorption from solution has even more applications than adsorption from the gas phase. Its importance in dyeing, photo-2

raphy, brewing, the purification of water, the clarification of oil and in making lubricants more effective is well known. Soils and soil colloids with their large surface areas (30 to 50 ac. per pound) are able by adsorption to remove from solution and retain fertilizer components essential to plant growth. Finally, the separation of components of a solution by liquid chromatography became important not only as an analytical tool for chemists but for separating out specific compounds from liquid solutions. For example, the aromatic, olefinic and paraffinic portions of liquid hydrocarbons can be separated by chromatography on a scale that promises to prove important in petroleum technology

Physical Adsorption of Gases and Vapours on Solids .-Physical adsorption resembles the condensation of gases to liquids. It depends upon the physical or van der Waals forces of attraction between the solid adsorbent and the adsorbate molecules. As one might expect for a given solid, the adsorption of a gas will become larger as the temperature at which the gas and solid are in contact decreases toward the boiling point of the gas or as the pressure of the gas at a given temperature is increased toward the pressure that would be necessary to actually condense it to a liquid. There is no chemical specificity in physical adsorption, any gas tending to be adsorbed on any solid if the temperature is sufficiently low or the pressure of the gas sufficiently high.

The five fundamental types of isotherms (plots of volume of gas adsorbed against pressure), which separately or in combination can describe the behaviour of all known examples of physica, ad-

sorption, are shown in fig. 1.

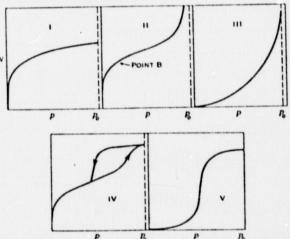


FIG. 1.-TYPES I. II. III. IV AND V ADSORPTION ISOTHERMS.

PLOT THE VOLUME OF GAS ADSORBED (AS MEASURED AT A STANDARD TEMPERATURE AND PRESSURE) IS PLOTTED AGAINST GAS PRESSURE, F. THE LIQUETACTION PRESSURE IS P.

Type I isotherms are representative of solids such as activated tharcoals, or natural or synthetic chabazites (q.v.) having very small pores (one to ten times the size of ordinary gas molecules) Type II isotherms are obtained on finely divided nonporous solids or on solids having fairly large pores, using as adsorbates mert cases such as nitrogen at temperatures close to their boiling points. Water vapour adsorbed on graphite yields a type III curve. scaptally believed that the heat of adsorption of the adsorbate to-decules for type III isotherms is equal to or a little smaller than the heat of liquefaction of the gas being studied. On solid adsorbits having all of their areas located on the walls of cracks or in, in size, isotherms of type IV Greeces smaller than about problem in in size, isotherms of type IV will normally be obtained. Finally, if the heat of adsorption is small but the pore size is also small, type V curves will be obtained as adsorption isotherms. Water vapour on charcoal gives such a curve provided the amount of surface oxide on the charcoal is telatively small.

Even though the chemical relationship of the gas and solid that is being studied is usually not important in determining the extert or nature of physical adsorption, a certain differentiation among the adsorbents can be made on a basis of the polarity of the solid or the adsorbate. For example, water vapour on graphite gives isotherms of type III, whereas nitrogen, argon, krypton and similar gases give type II isotherms. Apparently the exceptional behaviour of water vapour is to be attributed to the polar character of the -OH group and the nonpolar character of the carbon surface. On the other hand, polar solids such as silica gel adsorb water vapour even more strongly than adsorbates such as nitrozen.

Physical adsorption is characterized by low heats of adsorption and by rapid adsorption and desorption. The only systems in which physical adsorption is slow are those in which the pores are so small that an appreciable time is required for the ad-orbate molecules to diffuse down the pores or capillaries to the inner sur-

face on which they are finally to be adsorbed.

Numerous equations have been developed for representing the volume, v, of gas adsorbed as a function of pressure, p. One of these, the Langmuir equation, is of the form

Another, called the Freundlich equation, is

v= kp'/"

In these equations, a, b, k and n are constants. The Freundlich equation usually represents isotherms over certain restricted pressure ranges. At very low pressures or high temperatures the value of n approaches 1; at intermediate pressures, the constant 1/n assumes fractional values characteristic of the particular solid-gas system that is involved.

One of the more useful relationships for estimating the extent of adsorption at one temperature from that at another was due to M. Polanyi and his co-workers. In it the volume of gas adsorbed is plotted against the adsorption potential defined by the equation

adsorption potential = RTlnp. p

where po is the liquefaction pressure of the gas being studied. T is the temperature. R is the gas constant and p is the pressure at which the volume adsorbed (at a standard temperature and pressure) is being measured. Plots of such data show that except for a slight correction for the two-dimensional expansion of the adsorbed gas, the adsorption volumes taken at a series of temperatures and pressures will fall on a smooth curve.

In 1935 it was postulated that point B on type II isotherms for iron catalysts corresponded to a statistical monolayer of adsorbed gas and that the linear part of these isotherms and the portion convex to the pressure axis (to the right of point B in the type Il curve of fig. 1) represents the building up of multimolecular adsorption layers. A theory designed to explain the shape of these isotherms in terms of multimolecular layers may in its simplest

form be written 
$$\frac{x}{r(1-x)} = \frac{1}{r_m C} + \frac{(C-1)x}{r_m C}$$

where v is the volume of gas adsorbed at the relative pressure, x, of the adsorbate gas and C is a constant. A plot of the left side of the equation against the relative pressure, x, yields a straight line from which vm, the volume of gas in a monolayer, can be evaluated

This equation has become known as the Brunauer-Emmett-Teller or BET equation. A simple multiplication of vm by the cross-sectional area of each adsorbed molecule (as estimated from the density of the liquetical or solidified adsorbate) yields directly a value for the surface area of the solid in any convenient unit such as square metres per gram or acres per pound

One throw of physical adsorption assumes that in parous solids a considerable portion of the adsorbate is held by what is known as capillary condensation. To express the vapour pressure, p, of a liquid in a capillary, Lord Kelvin derived the equation

where  $\sigma$  is the surface tension of the liquefied adsorbate gas,  $\theta$ 

## E-121 ADSORPTION

is the contact angle between the liquid and the wall of the capillary, r is the radius of the capillary.  $\Gamma$  is the molal volume of the adsorbate and R, T and  $p_n$  are as defined above. The existence of capillary condensation is usually assumed to account for the hysteresis that is frequently found in adsorption isotherms representing physical adsorption of gases or vapours on porous solids (see type IV curve in fig. 1). By making proper allowance for the amount of monomolecular or multimolecular adsorption that occurs at a given relative pressure for a particular gas-solid system, it is possible to use the desorption isotherm of the type shown in fig. 1 for the type IV isotherm to calculate with the help of the Kelvin equation the pore size and the pore size distribution of capillaries.

This application of physical adsorption is one that is very valuable in studying the size of pores in catalysts and in other porous solids

Chemical Adsorption of Gases on Solids.—When certain specially prepared samples of porous iron are placed in contact with a mixture of the two simple gases hydrogen and nitrogen at a dull red heat and at high pressure, a chemical reaction takes place between the hydrogen and nitrogen to form ammonid. In this typical catalytic reaction it can be shown that both the hydrogen and nitrogen are capable of being adsorbed on the surface of the catalyst.

The temperatures involved (450° to 550° C.) are too high to permit physical adsorption to take place. It is concluded that the gases in this high-temperature range are held by chemical forces and hence by what has been called chemical adsorption or chemisorption.

Chemical adsorption occurs usually at higher temperatures than those at which physical adsorption occurs; furthermore, chemical adsorption is ordinarily a slower process than physical adsorption and like most chemical reactions frequently involves an energy of activation.

The heat of chemical adsorption is much higher than that of physical adsorption and corresponds to heats that are involved in chemical reaction.

Thus, for example, the heat of physical adsorption of nitrogen on an active iron synthetic ammonia catalyst at  $-195^\circ$  C. is in the range 1.360 to 3.000 cal. per mole of nitrogen compared with a liquefaction heat of 1.360 cal. per mole; in contrast with this the heat of adsorption of nitrogen at  $450^\circ$  C. on the same iron catalyst is about 35.000 cal. per mole of nitrogen. Chemical adsorption is perhaps most easily visualized as a surface compound between the atoms of the catalyst surface and the gaseous adsorbate formed under conditions which preclude the possibility of the adsorbate reacting with the main bulk of the catalyst to form a regular chemical compound.

As might be expected, chemisorption is chiefly of interest in connection with the occurrence of catalytic reactions. Apparently at least one of the reacting gases in a catalytic reaction has to be chemically adsorbed on the surface of the catalyst prior to reaction (see Catalysis).

One other application of chemisorption should be mentioned. It can be used to measure the surface concentration of components called promoters which are added to catalysts to the extent of a few per cent by weight to improve their activity. For example, the chemisorption of carbon monoxide by the iron atoms and of carbon dioxide by the alkali promoter has made it possible to ascertain that a few per cent of added promoter may cover as much as 50% to 75% of the surface of a doubly promoted iron synthetic ammonia catalyst.

Until relatively recently, little information was available as to the state of chemisorbed molecules on the surface of adsorbents. Only general inferences could be drawn based on the expected nature of interaction of the adsorbate and the adsorbent as judged by their respective chemical properties. In 1953 successful measurements were finally made of the infrared absorption bands of ammonia adsorbed on silica-alumina crucking activets and of carbon monoxide chemisorbed on such metals as iron, makel, cobalt, platinum and palladium. The information obtained from such spectra relative to the nature and the strength of the bonds hold-

ing the adsorbed molecules onto the surface without doubt opened an entirely new approach to a better understanding of chemisorphism

Adsorption in Solution.—When a substance (solute) is dissolved in a liquid (solvent) to form a solution, the solute usually tends to concentrate either in the surface or in the bulk of the solvent. For example, soap tends to concentrate preferentially in the surface of an aqueous soap solution (positive adsorption). Usthe other hand, inorganic salts, such as ordinary table salt, tend to concentrate in the bulk of an aqueous solution rather than in its surface (negative adsorption).

These qualitative observations have been expressed in a formal manner by the Gibbs adsorption equation

where  $\Gamma$  is the excess surface concentration of the solute in grammoles per square centimetre; c is the mean concentration of the solute;  $\delta\sigma/\delta c$  is the change of surface tension of the solution with the concentration of solute; and R and T are as defined above.

Adsorption From Solution by Solids.—The adsorption of a solute on the surface of a solid in contact with a solution is of fairly common occurrence. For example, activated carbon is used for removing coloured impurities from solution; clay can remove coloured components from oil; and bone char is used to remove impurities from sugar solutions in sugar refining.

The adsorption of solutes by added solids is generally explained according to the same Gibbs concept used for explaining the adsorption at a gas-liquid interface. However, it is much more difficult to measure surface tension at a liquid-solid interface. Accordingly, quantitative proof of the applicability of the Gibbs equation to adsorption from solution onto a liquid-solid interface is for the most part still lacking.

It is to be expected that the extent of adsorption from solution will depend on the nature of the solid adsorbent, the nature of the solute and the nature of the solvent. The detailed manner in which each of these influences the extent of adsorption is still not understood in spite of the large amount of research done on the subject in the first half of the both century. However, the influence of certain factors has been well documented and will now be briefly summarized.

The adsorption per gram will, for a given solid, increase with an increase in its accessible surface area. The accessible area, in turn, will for a given particle size depend upon the size and distribution of pores within the solid adsorbent. Since the adsorbate in a solution must reach the inner surface of a porous adsorbent by diffusion through capillaries filled with solvent, the amount of adsorption in any given time will depend on the nature

TABLE I.—Adsorption of Various Fally Acids on Charcoals of Different Peresities

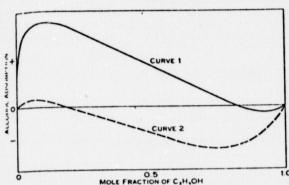
Weight ratio*		Propionic acid		Valeric acid		Enanthic scid	
		Per cent	Time for	Per cent	Time for		Time for
1.00		15	96 hr.	3	150 hr.	3	3 to he.
3,	: :	10	< the.	63	< ihr.	45	e the
.55		55	< 1 hr.	88	< the	05	< thr.

\*100 (1 weight ratio) is the percentage weight loss in the charcoal during activation fly or of orN axid and one god charcoal were used in each case. "Per centialise; tion" is the per cent of the added acted that is advorbed.

of the pores and capillaries as illustrated by the data in Table I (see M. Dubinin, Z. physik, Chem., 1931).

In the original unactivated material the pores were so small as to tend to screen out the larger molecules. With increased activation the charcoals increased their total adsorptive capacity and the pores became sufficiently enlarged to permit all of the solutes to be adsorbed regardless of molecular size.

It goes almost without saying that the time required to reach a given percentage of the final equilibrium values decreases as the pores become enlarged by activation. The rate of adsorption can be judged on thes@our charcoals by the time required to reach



FROM P. E. BARTELL, G. M. SCHEFFLER, AND C. E. SLOAM; "J. AM. CHEM. SOC." 53, 2501

FIG. 2 .-- THE ADSORPTION OF ETHYL ALCOHOL FROM A BENZENE SOLU. TION ON SILICA GEL (CURVE 1) AND ON CHARCOAL (CURVE 2). THE POSITIVE ADSORPTION REGION CORRESPONDS TO A HIGHER RATIO OF ALCOHOL TO BENZENE ON THE SURFACE THAN IN THE BULK LIQUID: THE NEGATIVE REGION. TO A LOWER RATIO

75% of the final equilibrium adsorption (see Table 1).

An excellent illustration of the influence of both solvent and solute is given by the data in Table II (see M. Dubinin and E. D. Zaverina, J. Phys. Chem. [U.S.S.R.], 1933).

TABLE II.—Adsorption\* of Fatty Acids From Water and From CCI, on Birch Charcoal

		From	water	From CC4		
Acid			1/4		0.115 .131 .433	
Formic Propionic	: :	0.316 .646 1.203	0.310	2.210 .851 .158		

\*The adsorption is given in terms of the constants & and 1/nof the Freundlich equation.

As is evident, the adsorption from water increases with the molecular weight of the acid, whereas from CCl, the extent of adsorption decreases with an increase in molecular weight. both solvents the adsorption increases as the solubility of the

Not only the nature of the solute and solvent but the actual composition of a solution has a strong influence on the extent and nature of the adsorption on an added solid. This is illustrated by the curves in fig. 2, taken from the work of F. E. Bartell, G. H. Scheffler and C. K. Sloan, J. Am. Chem. Soc. (1931).

The solid curve shows that on silica gel small amounts of ethanol are strongly adsorbed from a benzene solution. At high concentrations of ethanol, on the other hand, benzene is preferentially The dotted curve shows the corresponding adsorption isotherm for a sample of activated carbon. Clearly, the polar ethanol is relatively much more strongly adsorbed by silica gel than by activated carbon.

Attempts are sometimes made to list adsorbents in order of their efficiencies. However, the nature of the adsorbate, the presence or absence of a solvent, the concentration of adsorbate, the temperature and the surface area and pore size of a particular sample of adsorbent are all factors that can influence the efficiency of a civen chemical species of adsorbent. Reference should therefore be made to some of the comprehensive treatises for detailed information that would enable one to select the proper adsorbent

for a given adsorption problem. One special type of adsorption from solution merits special mention. It can be illustrated by zeolitic materials commonly ased in water softening. Certain ions such as Ca . Mg etc., are taken up by the zeolites. In the process, an equivalent amount of Na 1, 11 tor other ion is released to the solution. The resulting "adsorption" of the Ca to is really an exchange

teaction of the type

### 2NaX+Ca" = CaX2+2Na\*

where NaX represents the original zeolite or synthetic ion ex-

changer. Exchange adsorption does not represent a true adsorption in the strictest sense of the word. Nevertheless, it is ex tremely important in modern living and is fairly closely related

to adsorption.

Bibliography - S. Brunauer, The Adsorption of Gases and Vapors (1943); B. Trapnell, Chemisorption (1955); H. Freundlich, Colloid and Capillary Chemistry, trans. by H. S. Hatfield (1926); J. J. Bikerman, Surface Chemistry for Industrial Research (1947); A. E. Alexander and P. Johnson, Colloid Science, 2 vol. (1949); P. H. Emmett (ed.), Catalysis, vol. i (1954), vol. ii (1955); Chemical Society, Chemicorption (1957).

ADULLAM, a Canaanite city with a king (Josh. xii, 15) in the Shephelah (Josh, xv. 35), fortified by Rehoboam (II Chron. xi. 7) and still a place of importance at the time of the Maccabees (11 Macc. xii, 38). Its chief interest lies in its connection with David, who took refuge in its stronghold ("cave" is now generally admitted to be a scribal error; I Sam. xxii. 1); hence the allusion in the name Adullamites (q.v.) to seceders from a political party on some special issue. A site on the eastern edge of the Shephelah (Shefela) depression in southern Israel, in the neighbourhood of Socoh (Shuweikeh), seems to be indicated. Conjectural identifications have been (1) Khareitun in Jordan, southeast of Bethlehem, which has a large cave; (2) Deir ed-Dibban, about 6 mi. E. of Shuweikeh, where there are caves; and (3) 'Aid el-Ma' (an Arabic popular version of the name), south of Shuweikeh. The last identification is the one most favoured and the particular site is now held to be Tell esh-Sheikh Madhkur to the south of it.

See G. A. Smith, Historical Geography of the Holy Land, 25th ed.

ADULLAMITES is the name given to the English politicians who rebelled against their Liberal leaders and defeated the Reform bill of 1866, designed by Lord John Russell and W. E. Gladstone to enlarge the electorate by about 40%. These dissidents were aptly described by John Bright as a "political Cave of Adullam." attracting "every one that was in distress, and every one that was discontented." They eventually became about 40 strong: Russell's majority disappeared and his ministry resigned in June. Throughout a session remarkable for brilliance of debate and skill in parliamentary maneuver, the main attack upon the bill came from the Adullamites, a heterogeneous association with varying motives; and especially from Robert Lowe (later Viscount Sherbrooke, q.v.), who, according to Gladstone, "really supplied the whole brains of the opposition" and "had such a command of the House as has never in my recollection been surpassed."

Lowe's speeches form a classic statement of the view that democracy is inimical to good government. Such "distress" was genuine; but "discontent" was also important. Lowe and his lieutenants, E. Horsman and Bernal Osborne, were unrepentant Palmerstonians with frustrated ambitions, who resented the mounting influence of Gladstone and the radicalism of Bright in the Liberal party. Powerfully supported by John Thadeus Delane  $(q, x, \cdot)$  in the Times, they could rely upon "a last rally of aristocrats of the Whig decadence," in which heirs to peerages, notably Lord Elcho and Lord Grosvenor, played a prominent part; and they were followed by certain members for small constituencies who feared the loss of their seats.

The Adullamite revolt was symptomatic of the divisions within Liberalism after Lord Palmerston's death, and foreshadoved later secessions to Conservatism. However, its success was short-lived and the group soon dissolved. Popular demand for reform, previously limited, had been sharply stimulated by the bill's defeat; and in 1867 their recent ally, Benjamin Disraeli, passed a much (A 1. T.) more drastic measure, the second Reform act.

ADULT EDUCATION, in its broadest sense, signifies any s or provided for mature men women. Because of the scope of this meaning, the term has had many special interpretations, each built on a conception of the learning process, a historical movement or an institutional pattern.

Adult education deals with that whole span of life which begins when childhood is left behind and continues until death. The mature person passes through several stages that are perhaps as clearly differentiated as are the various periods of childhood. He lives in a social climate that influences his values and shapes the methEncyclopedia Britannica, 1971 Edition, pp. 47, 353-55

"Royal Society of London for improving natural knowledge," and the charter of incorporation granted by Charles II named Boyle a member of the council. In 1680 he was elected president of the society, but declined the honour from a scruple about oaths. In 1668 he moved to London, where he died on Dec. 30,

Boyle's great merit as a scientific investigator is that he carried out the principles which Bacon preached in the Novum Organum. Yet he would not avow himself a follower of Bacon or indeed of any other teacher. He performed experiments in the hope of effecting the transmutation of metals, and he was instrumental in obtaining the repeal, in 1689, of the statute of Henry IV against multiplying gold and silver. With all the important work he accomplished in physics-the enunciation of Boyle's law, the discovery of the part taken by air in the propagation of sound, and investigations on the expansive force of freezing water, on specific gravities and refractive powers, on crystals, on electricity, on colour, on hydrostatics, etc .- chemistry was his peculiar and favourite study. His first book on the subject was The Sceptical Chemist, published in 1661, in which he criticized the "experiments whereby vulgar Spagyrists are wont to endeavour to evince their Salt, Sulphur and Mercury to be the true Principles of He advanced toward the view that matter was ultimately composed of "corpuscles" of various sorts and sizes capable of arranging themselves into groups, and that each group constituted a chemical substance. He distinguished between mixtures and compounds and showed that a compound might have different qualities from those of its constituents. He studied the chemistry of combustion and of respiration and made experiments in physiology, where, however, he was hampered by the "tenderness of his nature" which kept him from anatomical dissections.

Besides being a busy natural philosopher, Boyle was interested in theology, and in 1665 would have received the provostship of Eton, if he had taken orders. He learned Hebrew, Greek and Syriac in order to pursue his scriptural studies and spent large sums on biblical translations. By his will he founded the Boyle lectures, for proving the Christian religion against "notorious infidels, viz., atheists, theists, pagans, Jews and Mahommedans," with the proviso that controversies between Christians were not to be mentioned.

(See also CHEMISTRY: History of Chemistry.)

An incomplete and unauthorized edition of Boyle's works was published at Geneva in 1677, but the first complete edition was that of Thomas Birch, with a life, published in 1744, in five folio volumes, a second edition appearing in 1772 in six volumes, quarto. Boyle bequeathed his natural history collections to the Royal society, which also possesses a portrait of him by the German painter, Friedrich Kerseboom (1632-90).

See also references under "Boyle, Robert" in the Index.

See F. Masson, Robert Boyle, a Biography (1914); L. T. More, Life and Works of the Honourable Robert Boyle (1944).

BOYLE (MAINISTIR NA BUILLE), a town in County Roscommon, Republic of Ireland, 106 mi. W.N.W. of Dublin and 24 mi. S.S.E. of Sligo by road. Pop. (1961) 1,739. It is situated on both banks of the Boyle, a tributary of the Shannon, between Loughs Gara and Key, at the foot of the Curlew hills. Three bridges connect the two parts of the town. Trade is mainly agreentured.

To the north of the town stand the extensive ruins of a Cistercian abbey founded in 1161 and suppressed in 1569, including remains of a cruciform church, with early Gothic and Romanesque arches carved in beautiful detail down the long nave. There is a large dolmen by the road toward Lough Gara; many prehistoric remains, including dugout boats, have been found in the lake. Boyle was incorporated by James I.

BOYLE'S LAW, a relation, discovered by Robert Boyle, between the pressure, p, and the volume, v, of a gas, viz., pv = constant, at constant temperature. See Boyle, Kobert, Kinetic Theory of Matter: The Gas Laws; Thermodynamics: Applications to Medical Cause, Electricity, Royle's Law.

tions to Ideal Gases; ELASTICITY: Boyle's Law.
BOYLESVE, RENÉ (real name RENÉ MARIE AUGUSTE

TARDIVEAU) (1867-1926), French novelist who influenced many other writers, including Proust, was born in La Haye-Descartes (Indreet-Loire), April 14, 1867, and was educated in Poitiers, Tours and Paris. His studies of both liberal and fine arts, science and law did not lead to his entering a profession. After ten years in unimportant jobs, he wrote, under his mother's maiden name, his first novel, Le Médecin des dames de Néans (1896), in which the essential Boylesve is already to be found, and which anticipated Proust in style. There followed Le Parfum des iles Borromées (1898), a bitter book which he softened in tone and cut by nearly half in the definitive edition (1907). Sainte-Marie-des-Fleurs, an autobiographical love story, had appeared in 1897. Then came the powerful series known as the romans tourangeaux-Mademoiselle Cloque (1899), La Becquée (1901), L'Enfant à la balustrade (1903; Eng. trans. The Child at the Balustrade, 1929) and La Jeune Fille bien élevée (1909)-which, although ostensibly works of imagination, reveal Boylesve as the historian par excellence of rural and urban society in the west of France during 1870-1900a historian and, at the same time, a poet.

Mention should also be made of his most famous and least understood work. La Lecon d'amour dans un parc (1902), which purports to be the daring story of an 18th-century love affair, but is fundamentally a novel about a child's education. His least known work, Le Bel Avenir (1905), is of interest because it was always his own favourite. His last novels were Mon Amour (1908), Le Meilleur Ami (1909) and Madeleine jeune femme (1912; Eng. trans. A Gentlewoman of France, 1916) which is probably his masterpiece, though not his most attractive work. He also wrote many short stories, collected in La Marchande de petits pains pour les canards (1909) and Bonheur à cinq sous (1917). Boylesve was elected to the Académie Française in 1918. He died, Jan. 14, 1926, in Paris. Among his posthumous works are Opinions sur le roman (1929) and Feuilles tombées, ed. by E. Gérard-Gailly (1927)—the latter an important fragment of his private journal, which shows rare critical and introspective gifts, and Profils littéraires (1961). (E: G.-GA.)

BOYNE (AN BOINN), a river in the Republic of Ireland rising in the Bog of Allen, near Carbury in County Kildare, and flowing in a northeasterly direction past Trim, Navan and Slane to enter the Irish sea 4 mi. below Drogheda. With a total length of 70 mi., it is noted for its salmon fishing and its lower reaches are navigable by coastal shipping. It figures largely in Irish history. The Bronze Age burial tumuli at Knowth, Newgrange and Dowth along its course are of the highest archaeological interest and importance. Slane is intimately associated with St. Patrick and with the introduction of Christianity to nearby Tara, the seat of the Irish kings.

Battle of the Boyne .- On July 11 (new style; July 1, old style), 1690, the forces of King William III and the former king James II came to battle on its banks. James, failing to take Derry and Enniskillen, had left Ulster as a bridgehead to William and had wasted his best Irish regiments in England and France. He assembled in the Oldbridge area, south of the Boyne, 7,000 French infantry, some regular Irish cavalry and untrained Irish infantry and dragoons-altogether about 21,000 men. William led the Dutch Blue Guards, two regiments of French Huguenots, some English, and contingents of Danish, Prussian, Finnish and Swiss mercenaries-altogether about 35,000 men. Fearing encirclement by William's cavalry which crossed the Boyne at Rosnaree on the left and at Oldbridge toward the right, James fled hastily from the battle and from the country. The battle was William's but the Jacobite army successfully withdrew to carry on the war for another year in Ireland. The battle of the Boyne is celebrated in northern Ireland by Orangemen as a victory for the Protestant cause on July 12, which is actually the old style date of the more decisive battle of Aughrim (q.v.). See GRAND ALLIANCE, WAR OF (U. G. F.)

BOYS' BRIGADE, THE, was founded on Oct. 4, 1883, by William Alexander Smith (1854-1914) for "the advancement of Christ's Kingdom canong lays, and the premotion of habits of Obedience, Reverence, Discipline, Self-respect and all that tends toward a true Christian manliness." As secretary of the Sunday school of the Free College Church mission in Glasgow, Scot., Smith



These two simplifying facts bring the properties of te of matter within the range of mathematical treatment. The etic theory of gases attempts to account, in terms of the moular structure of matter, for all the nonchemical and nonctrical properties of gases. A brief statement of the methods d results of the kinetic theory of gases will be given first, folsed by a brief consideration of the kinetic theory of matter in e solid or liquid state.

#### THE KINETIC THEORY OF GASES

One of the earliest triumphs of the kinetic theory was its exanation of the laws that had been found to connect the density, essure and temperature of a gas. The kinetic theory regards a ass of gas as a collection of independently moving molecules; if ese are shut up in a closed vessel, molecules must continually dlide with the walls of the vessel, exerting pressure at the moment collision, and the kinetic theory interprets the pressure of the s as the aggregate of the pressures exerted by the various moleiles when they collide with the boundary. A quantitative rela-on between the pressure and the molecular velocities is easily sained.

is will be moving in different ways, but they can be divided up to a system of showers, such that all the molecules in any one lower have approximately the same velocity and are moving in e same direction. Let u, v, w denote the components of the elocity of any molecule in three directions at right angles in nce, and let us fix our attention on any one shower, whose polecules have components u1, v1, w1. Let us consider the impact i the molecules of this shower upon an area S of the boundary is the containing vessel, and for simplicity let S be perpendicular the direction of u. Then each molecule of the shower that trikes the area gives up momentum mu to it before its motion the w direction is arrested, and as it rebounds with equal elocity it also acquires momentum mu in the opposite direction, o that the total transfer of momentum is 2mu. The number of nolecules belonging to the shower that strikes the area S in a mall interval of time dt is equal to the number that lay within distance u,dt of S at the beginning of this interval and so ocepied a small disk of volume Suidt of the gas. If there are vi polecules in unit volume belonging to the shower, the number nside the disk was Suzvidt.

Thus these molecules transfer momentum 2mu12v1Sdt to the trea S of the boundary; and the total momentum so transferred y the molecules of all showers can be written

where the sum includes a term for each shower whose molecules the moving with a component u directed toward S. The sum also be written & v U2 where v is the total number of moleteles in unit volume and U2 denotes the average value of u2 for the different molecules; the factor \frac{1}{2} is introduced because all of all the showers will be moving with a component it directed away from S and hence cannot contribute to the pressure S. Or, let  $C^2$  stand for the average value of  $u^2 + v^2 + w^2$ , or the square of the actual velocity, for all the molecules. Since many molecules will be moving in one direction as in another, e average values of u2, v2 and w2 will be the same. Hence = 1 C2; and the momentum transferred to the area S during Le interval dt is } mv SC2dt.

Since the momentum transferred must be equal to pSdt, where I is the pressure or force per unit area on the boundary, the L'ue of p is

it. since mr is the total mass in unit volume and hence equals he density p, expressed in grams per cubic centimetre,

$$p = \frac{1}{2}\rho C^2$$
 (2)

Since  $\rho$  and  $\rho$  can be measured for any gas, the value of C can be calculated. C is called the root-mean-square velocity of

gaseous if all the molecules were moving v the velocity C. The distribution of the molecular velocities will be considered presently. Some values of C at 15° C. are as follows:

> Mercury vapour Hydrogen Air C in cm. per sec. C in ft. per sec. 188.800 1,634 18,930 6,190

> The Gas Laws.-It was found by Boyle that as a gas is compressed without change of its temperature its pressure increases directly as its density. This conclusion follows from formula (2) if the assumption is made that C2 depends only on the temperature. The latter assumption can be shown to be a consequence of the laws of dynamics.

> Furthermore, it was shown by J. A. C. Charles and by J. L. Gay-Lussac that when a gas is heated at constant volume its pressure increases at a rate that is the same for all gases. The pressure increases, in fact, in proportion to the thermodynamic absolute temperature T, as can be shown by a thermodynamical argument. Thus the laws for a gas as established by observation can be expressed in the single formula

$$\phi = \rho RT$$
 (3)

Calculation of the Pressure in a Gas .- The molecules of a where R is a constant depending upon the kind of gas, or, as the equation is more commonly written,

$$pv = RT$$
 (4)

where v equals 1/p and represents the specific volume or the volume of a gram. Let T be expressed in degrees Celsius (centi-

Comparison of formulas (2) and (3) shows that

$$C^2=3$$
 RT (5)

Thus the average velocity of the molecules varies in proportion to the square root of the absolute temperature.

The Specific Heat .- The total kinetic energy of translation of all the molecules in unit volume is v(1mC2) or 1pC2 or pRT. Since p represents the mass in unit volume, the energy in unit mass is & RT. This energy increases by the amount & R when the temperature is increased by one degree. Hence the specific heat of a gas at constant volume should be & R, provided the molecules contain no variable energy other than that associated with the motion of translation.

The specific heat at constant volume is found by experiment to equal & R or \$ pv/T for helium and the other rare gases, whose molecules consist of a single atom. For gases with polyatomic molecules, the specific heat exceeds \( \frac{1}{2} \) R except at extremely low temperatures. The difference is ascribed to the existence of energy of rotation of the molecules, or of vibration of the atoms in gases having polyatomic molecules.

The Equipartition of Energy .-- According to a famous principle known as the equipartition of energy, when a dynamical system is in statistical equilibrium at a given temperature T, the same amount of average kinetic energy is associated with each degree of freedom; i.e., each independent mode of motion of the system. A molecule in translation has three degrees of freedom corresponding to the three mutually perpendicular directions in which it can move independently. It follows that in gases composed of different kinds of molecules, the average translational energies of the molecules, or the values of  $\frac{1}{2}mC^2$ , should be the same for all the different kinds of molecules. When the molecules are actually mixed together, this conclusion can be verified by an analysis of the effects of their collisions with each other. Even if the different kinds of molecules are in different vessels, the same conclusion can be reached by a more abstruse argument

based upon the Newtonian or "classical" laws of dynamics.

Since C2 has been found to be proportional to the absolute temperature T, it is possible to write for the average translational energy of a molecule

where k is a constant of proportionality. The average kinetic energy for each degree of freedom, according to the principle of molecules; the pressure would be the same as it actually is equipartition, is then a third of \( \frac{1}{m}C^2 \) or \( \frac{1}{k}T \). Since C<sup>2</sup>

# KINETIC THEORY OF MATTER

equals 3RT, it is seen that k=mR. The numerical magnitude of k, which is known as the Boltzmann constant or the "gas constant for one molecule," is  $1.38044 \times 10^{-16}$  in centimetre-gramsecond units.

Soon after 1925, however, it came to be realized that the classical laws of dynamics represent only an approximation, which is close to the truth in dealing with masses that are sufficiently large, or moving sufficiently rapidly, or subjected to sufficiently weak forces. The classical laws, one of which has just been used in calculating the pressure in a gas, are sufficiently accurate for a description of the translational motion of the molecules in a gas; but they fail badly in dealing with the rotational and vibrational motions of the molecules. An adequate theory of the specific heat of gases composed of polyatomic molecules must be based upon the newer quantum or wave mechanics.

Counting the Molecules.—Since, as has just been seen, the quantity  $\frac{1}{2}mC^2$  has the same value for all gases at a given temperature, it follows from formula (1) that the number of molecules in unit volume or  $\nu$  is the same for all gases at the same temperature and pressure. This remarkable fact is known

as Avogadro's law (see Avogadro's Constant.)

The kinetic theory of gases does not furnish any reliable method of ascertaining the numerical value of v. The best method is to start from the well-attested fact that in electrolysis each atom of hydrogen carries an electric charge numerically equal to the charge on an electron, which has been measured. The total amount of electric charge delivered by a gram of hydrogen in being deposited electrolytically is also known. ELECTRICITY, CONDUCTION OF: Conduction in Liquids.) charge on a gram divided by the charge on an atom then gives the number of atoms in a gram of hydrogen; and this number, divided by 2, is the number of molecules in a gram of hydrogen gas. This number again, multiplied in turn by the density or the mass in unit volume, gives the number of molecules in unit volume or v. It is thus found that in a gas under a pressure of one atmosphere and at a temperature of 0° C.,

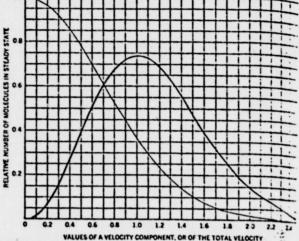
In a similar way it is found that the number of molecules in a gram-molecule of any substance is  $N_0 = 6.02 \times 10^{23}$ . This is an enormous number.

The Law of Distribution of Molecular Velocities.—The molecules of a gas are not all moving with the same velocity. When the gas is at rest and free from disturbance, the effect of collisions between its molecules was shown by J. C. Maxwell and L. Boltzmann to be such that the molecular velocities soon come to be distributed in a definite manner. The gas is then in a steady or normal state. When this state has been attained, the statistical equilibrium is actually maintained in a very simple manner. Let us divide all possible velocities into distinct ranges a, b, c. . . . . When two molecules moving with velocities a,b collide, the collision changes the motion of both and they assume new velocities p,q. Thus the collision takes one molecule away from each of the classes a,b and adds one to each of the classes p,q. When the gas is in its steady state, there occur just as many collisions of the inverse type, in which a molecule is taken from each of the classes p,q and added to one of the classes a,b. The statistical effect of the collisions is thus nil.

The distribution of the molecular velocities in the steady state

may be described as in fig. 1.

Confining our attention to one component of velocity u, it is found that the values of u for the different molecules conform to what is called the law of trial and error—they are distributed at random around the value u = 0 according to the same law that determines the distribution of shots around the middle point of a line-target. To express the result mathematically, if u, v, w denote the three components of velocity in three directions at right angles in space, then the number of molecules whose velocity is such that



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FIG. 1.—THE LAW OF DISTRIBUTION OF VELOCITIES. THIN CURVE INC.
CATES NUMBER OF HOLECULES IN STEADY STATE FOR EACH VALUE :
VELOCITY COMPONENT. THICK CURVE INDICATES NUMBER OF MOLICILITY
IN STEADY STATE FOR EACH VALUE OF THE TOTAL VELOCITY

is found to be 
$$N\left(\frac{hm}{\pi}\right)^{\frac{1}{6}-hm(w^2+v^2+w^2)} du dv dw$$

Here N is the total number of molecules and m is the raw of each, while h is a constant, which will be found to depend a the temperature. This law is commonly known as Maxwell's in of distribution of velocities.

If we fix our attention on any one component of velocity, u, disregarding the values of v and w entirely, it is found the number of molecules for which this component lies between u and u+du is

$$N\left(\frac{hm}{\pi}\right)^{\frac{1}{4}}e^{-hmu^2}du$$

This partition of values of u is shown graphically in the curve in fig. 1. The numbers along the horizontal axis representations values of u, and the corresponding height of the thin cure: proportional to the total number of molecules that have = particular value of u in Maxwell's steady state. The whole 13 under this curve is equal to 100 va, or 177.25, of the small square Let us, for instance, suppose that each of these small square represents a million molecules; then we find that in a gas -177,250,000 molecules, rather less than 20,000,000 have value: u between 0 and 0.1, about 19,500,000 have values of a terms 0.1 and 0.2 and so on, while less than a million have 12between 1.7 and 1.8, and less than 40,000 have values terris 2.4 and 2.5. These values of u are measured on an arisescale that has not yet been determined. But whatever the on which u is measured, we see that high values of u are " rare, the majority of molecules keep to moderate values and favourite value of all is zero.

In many problems the total velocity of a molecule is of simportance than its individual components. If  $c^2$  is written  $u^2+v^2+w^2$ , so that c is the total velocity of a molecule. Freadily be deduced from formula (6) that the total number molecules for which c lies between c and c+dc is

This distribution of velocities is represented graphically thick curve in fig. 1. We see that both very high and velocities of c are now rare, the favourite value for c being c

From formula (8) it can be shown by integration that average of the square of the velocity of the molecules, which previously denoted by C<sup>2</sup>, is also equal to 3/(2hm). Since:

solute temperature T, it follows that .

$$h = \frac{1}{2kT}$$

Dalton's Law.-Imagine that a gas consists of a mixture of pses of different kinds, so that unit volume contains a mass p ef one kind, p. of another and so on. The pressure on the bundary is now the sum of the pressures exerted by molecules of all kinds. The pressure exerted by the first kind is piRT, that by the second kind is paRT and so on; hence the total pressure is given by

$$p = \rho_1 RT + \rho_2 RT + \dots = \rho RT$$

where  $\rho$  equals  $\rho_1 + \rho_2 + \dots$  and represents the total mass in mit volume. This formula shows that the pressure of a mixture of gases equals the sum of the pressures that would be exerted separately by the several constituents if each were present alone.

Brownian Movement.—From the value  $k = 1.38 \times 10^{-16}$  it is readily calculated that a molecule, or aggregation of molecules, of mass 10-12 grams ought to have a mean velocity of about 2 mm. a second at 0° C. Such a velocity ought accordingly to be set in a particle of 10<sup>-12</sup> grams mass immersed in air or liquid at C., by the continual jostling of the surrounding molecules or particles. A particle of this mass is easily visible microscopically, and a velocity of 2 mm. per second would of course be visible if tratinued for a sufficient length of time. Each bombardment will, however, change the motion of the particle, so that changes are too frequent for the separate motions to be individually visible. But it can be shown that from the aggregation of these separate short motions the particle ought to have a resultant notion, described with an average velocity which, although much smaller than 2 mm. a second, ought still to be microscopically visible. R. von S. Smoluchowski and Albert Einstein have shown that this theoretically predicted motion is simply that seen in the Brownian movement" first observed by the botanist Robert Brown in 1827. From observations of the motion, values of and No can be deduced that are in fair agreement with those found by the method previously described. Thus the Brownian notion provides visual demonstration of the reality of the heat motion postulated by the kinetic theory. (See Brownian Move-MENT.)

Correction of the Gas Equation .- The laws that have just been stated are obeyed very approximately, but not with perfect Emperature too low. Van der Waals in 1873 ascribed the imperfections of the foregoing formula for the pressure to two

1. The calculation has not allowed for the finite size of the colecules, and their consequent interference with one another's

2. The calculation has not allowed for the attractive force between the molecules, which, although small, is known to have a real existence. The presence of this force results in the molecules, bea they reach the boundary, being acted on by forces in additoo to those originating in their impact with the boundary.

To allow for the first of these two factors, on the assumption Lit a molecule is a hard elastic sphere, Van der Waals found that v in formula (4) should be replaced by v - b where b is four times the aggregate volume occupied by all the molecules in a tan; to allow for the second factor, on the assumption that the Exaction is weak, he replaced p by  $p + a/v^2$  where a is a new astant. He thus obtained for the pressure-volume relation the Laws equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Lich is known as Van der Waals's equation.

This equation has the great advantage that it predicts a gental behaviour of gases under high pressure similar to that which \* actually observed. (See Low-Temperature Physics.) can be assigned to a and b that make the equation fit the observa-

also equals \$kT in terms of the Boltzmann constant k and the tions roughly, but it cannot be made to fit exactly for any Several reasons are recognized for the limited success of Van der Waals's equation. The principal one is that the molecules are not clastic solids and cannot even be said really to possess a definite size. When not too close together, two molecules attract each other; as they approach, this attraction increases to a maximum, then decreases to zero and is replaced by a rapidly mounting repulsion. Because of this strong repulsion when close together, the molecules behave in many respects as if they were hard objects having a certain size and shape. The equivalence is not exact, however, and no simple formula can be written to represent exactly the relation between p,v and T. In dealing with certain other phenomena in gases it is convenient to make the same arbitrary assumption that the molecules are small elastic spheres. The properties of such an elastic-sphere gas can then be deduced, and they are found to agree in large measure, although never exactly, with the properties of actual gases.

The Free Path in a Gas .- Let us regard each molecule of a gas provisionally as a small round shot. Each shot travels on in a straight line until it strikes some sort of target, after which its speed is changed and its direction of motion altered. Some molecules strike the target formed by the boundary of the vessel containing the gas; others strike another molecule. If the diameter of each molecule is  $\sigma$ , two molecules cannot pass so close that the distance between their centres is less than o without a collision taking place, so that each molecule can be regarded as forming a target of area mo2. If there are v molecules per unit volume, the number in a small layer of thickness t and cross section S is viS, and these form a target of total area #o2viS. This quantity is proportional to t, and for a certain value of t it becomes equal to S. When t has this value, the target formed by the combined molecules precisely fills up the whole area S, so that no molecule can get through without a collision. The value of t which makes πσ²νtS equal to 5 is

$$l = \frac{1}{\pi \nu \sigma^2}$$

so that in traveling through a layer of this thickness in the gas each molecule will collide with some other molecule and have its speed and direction of motion changed.

The foregoing simple calculation requires adjustment, however, in several respects. The molecules are distributed irregularly in space, and allowance must also be made for the variation in their velocities. An exact calculation, first given by Maxwell, shows that the average distance *l* which a molecule travels before colliding with another molecule is given by

$$l = \frac{1}{\sqrt{2 \pi \nu \sigma^2}} \tag{9}$$

In ordinary air the length of the average free path is 0.000006 cm. or 400.000 of an inch. Since the molecule of air travels at a rate of 50,000 cm. a second, it must describe 8,000,-000,000 free paths every second, and so collides with 8,000,000,oco other molecules in each second of its existence.

The individual free paths between collisions will be distributed statistically on both sides of I. The favourite length of free path is actually zero; in this case, a molecule stands almost still until another one strikes it. The frequency of free paths of a given

length decreases as the length increases, and paths several times as long as the average length !

are rare. (See fig. 2.)
Conduction of Heat.—During the description of any free path the energy of a molecule remains unchanged, although it may gain or lose energy at a collision with another molecule. Consider the motions of molecules in a gas in which the temperature is not uniform. Let one layer AB of the gas be at a

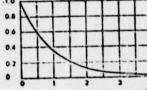


FIG. 2 .-- THE CURVE REPRESENTS THE RELATIVE NUMBERS OF MOLEC. ULAR FREE PATHS OF VARIOUS LENGTHS. THE LLNGTH IS EX-PRESSED IN TERMS OF THE AVER-AGE LENGTH AS A UNIT

# DEFENDANTS' EXHIBIT TTT

That portion of Kahn Affidavit, filed June 27, 1968, designated Exhibit 120

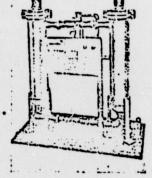


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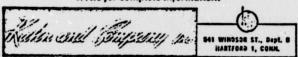


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January through October, 1958

DEFENDANTS' EXHIBIT M(5)

11. Erdmann U.S. Patent No. 2,254,799

Sopt. 2, 1941.

K. ERDMANN
PROCESS FOR THE HOUSEN OF CAMBON MONEXIDE FROM
MIXICISES THEREOF WITH HYDROGEN
Filed April 22, 1939

GAS HOLDER 7, CO 5 (3) 8 11 CONVERTER DAS 71-3 10 17 19 COMPRESSOR 2 37.68} 37. 63) 13 21

d Erdmann

#### BATEMT STATES HIMITED

2.254.799

PROCESS FOR THE DEMOVAL OF CARBON MONORTHE FROM METURES THEREOF MONONIDE FROM

Konrad Erdmann, Radenthein, Germany, as-signer to American Magnesium Metals Corpo-ration, Pittsburgh, Pa.

Application April 22, 1939, Serial No. 269,365 In Germany May 7, 1938

4 Claims. (Cl. 183-4)

This invention relates to a process for the removal of carbon monoxide from mixtures there-

of with hydrogen.

For the removal of carbon monoxide from mixtures thereof with hydrogen the technical process principally employs the reaction of the car-bon monoxide with steam, to form carbon dioxide and hydrogen (water gas oxidation). Another large scale technical process for the separation of such gaseous mixtures depends upon 10 fractional description with the aid of a reduction liquefaction by cooling to a low temperature. of pressure whereby the adsorption agent re-Various other processes such as preferential oxidation of carbon monexide with oxygen, reduction to methane or methanol, adsorption with copper salt solutions or with caustic soda solu- 15 tiers are employed especially in order to remove by subsequent purification the residual quantitles of carbon monexide which remain behind after most of the carbon monoxide has been removed in the aforesaid large scale technical 20 processes. The selective adsorption on solid substances of large surface which stands so very much in the foreground in other fields has hitherio not proved suitable for the separation of carbon monoxide and hydrogen. Perley does indeed state (see U. S. A. specification No. 1,596,916) that certain metal oxide gels are capable of selectively adsorbing the carbon monoxide and carbon dionide from a water gas mixture so that on charsing these adsorbents to saturation technically pure hydrogen passes through unbound. By driving out the adsorbate with the aid of a reduction of pressure which is preferably followed by an activation of the gels with hot air a mixture of carbon monoxide and carbon dioxide in the ratio of 8:1 is said to be recovered, which only contains traces of hydrogen, miregen and oxygen. Perley mentions as suitable adsorbents, the colloidal oxides of the metals titanium, zirconium, vanadium, columbium, thorium, molybdenum, chromium, manganese, iron, cobalt, nickel, copper, beryllium, magnesium and the rare earths. This process has not however been utilised commercially (see "Das Kohlenoxyd" Dr. Jurgen Schmidt, Leipzig, Akadem. Verlagages., 1935, p. 73); even if it were capable of being carried out with the result indicated, the lack of technical success has apparently been due to the necessity of employing colloidal metal oxides, the life of which as adsorbents is further shortened by the intermediate heating. It is not possible to replace the metal oxide gels in this process by insensitive adsorbents of the type of active carbor, because the adsorption constants of the two gases in relation to active carbon lie 55 charging operation long before the adsorption

too near to one another at low working temperatures.

A process has been proposed for the separation of hydrogen and carbon monoxide with the ald of adsorption agents of the type of active carbon or of silica gel. In this process the mixture of the two gases is forced into the adsorption agents in the original proportion of the components and a separation or enrichment is only produced by leases the gas mixture with reduction of pressure in such a way that in the first fractions the difficuitly adsorbable hydrogen predominates, while in the last fractions the more readily adsorbable carbon monoxide predominates. In contradistinction to this, by the present inventior, the problem is solved of separating mixtures of hy-dregen and carbon monoride with the ald of active charcoal or adsorption charcoal, so-called A-carbon, the most custom my and cheapest adsorbent, by selective adsorption, hence to attain the object that the carbon monoxide is preferentially retained on charging whilst a very considerable proportion of the gas mixture flows away unbound in this werking stage as a fraction rich in hydrogen, whereupon one or more fractions, in which the carbon monoxide is enriched, are released by driving out the adsorbate with the aid of pressure reduction which the above process employs exclusively for the separation of the two gases.

The present process has the advantage that it does not equire the use of high pressure-tight 35 apparatus; that moreover 50-95% of the thermal energy expended can be recovered whereby moreover the cooling is from the outret cheaper than compression. Moreover, the process is also su-perior in its results to the known processes, espe-40 cially as regards the enrichment of the hydrogen.

Accordingly, it is the main object of this invention to provide a process for the removal of carbon menoxide from gaseous mixtures con-taining it accompanied with hydrogen, with the 45 aid of selective adsorption on active carbon.

Another object of the invention is to provide a process of this kind which requires only a small quantity of adsorption agent and ensures a gentle treatment of the same, both these circumstances contributing to the economy of the 50 process.

It has been possible to obtain these objects in that the charging of the adsorption agents proceeding at low temperatures is broken off in each

equilibrium is attained. So long as the carbon is still fully adeceptive, the hydrogen passing through contains very small quantities or carben moneride, while with increasing saturation the curve of the carbon monoxide content increases steeply until the adsorption equilibrium is attained. The duration of the charging steps is therefore kept as short as possible. The adis attained. The adsorbate may be completely driven out in a few minutes by appropriate reduced pressure; even if only two ansorption chambers are provided, which are set in operation alternately, the charging and de-charging steps can be caused to alternate in a period of time of the order of minutes.

If the further messure is employed of undertaking the pressure reduction in two or more steps and thus collecting the describate set free separately, as is known per se, then also a fraction relatively poor in carbon monoxide may be 20 separated as first running before the components rich in carbon monoxide have been driven out. This first running is advantageously led back into the starting mixture before the latter enters the adsorption chamber.

An embediment of the invention will now be

described by way of example: A mixture of 93% of hydrogen with 7% of carbon monoxide cooled to -50° C. is led over an active charcoal which is pre-cooled to -50° C. 30 Assuming that under the working conditions chosen (velocity of gas flow and the like), the adsorption equilibrium characteristic for this gas mixture is set up after 10 minutes, that is that after a charging time of 10 minutes the gas 35 emerges with the same carbon monoxide content with which the starting mixture enters, then the mean value of the carbon monoxide content of the hydrogen freely passing through during an entire charging process would amount to 40 about 4.5%. In the first minutes however a more considerable proportion of hydrogen with 1 to 2% of carbon monoxide escapes from the adsorption chamber. If the change from the conditions of charging to the condition of driving off is allowed to occur regularly at this point of time then the overwhelmingly prependerating quantity of hydrogen with 1 to 2% of carbon monoxide can be obtained in the adsorption phase as an unbound component. When decharging by suction when the pressure is gradually and the pressure is gradually and the pressure of 100 mms. ually reduced to a reduced pressure of 100 mms. 50% by volume of a mixture is released, the carbon monoxide content of which is about equal to that of the starting mixture. Upon further 55 reduction of the pressure to 10 mms, the carbon monoxide content in the desorbate increases steeply with reduction of pressure so that the mean value of the CO concentration in the remaining 50% by volume is nearly 10 times greater than the content in the starting mixture. By frectional description the describate can be de-composed into these two fractions, the first of which is advantageously led back into the start-ing mixture in the path of this mixture to the 65 adsorption chamber. If the whole describate is collected together then its CO content amounts to about 38%.

The main portion of hydrogen with 1-2% of carbon monoxide passing through unbound may if desired be brought to a lower carbon monoxide content or entirely freed from carbon monoxide by treatment according to any known chemical

monoxide is freed, preferably by water gas oxid tion, from carbon monoaide to the desired residnal content, or carbon monoxide is entracted therefrom by liquefaction by cooling to a low temperature, or by treatment with copper sait solution. After cutting off the vacuum pump, the active carbon is ready for adsorbing the next charge without a special re-activation being charge without a special re-activation being necessary. It is sufficient from time to time, may be after 159 to 209 working days, to free the adsorbent by geatle heating (for example to 70° C.) from the admixtures retained which are solid at the working temperature and do not possess a sufficiently high vapor pressure in order to be removed by reduced pressure (for example water). Hence it is advantageous to work with three adsorption chambers, each of which is pro-vided with devices for heating and cooling.

The circumstance, that as a result of the rapid alternation of the charging and de-charging periods the quantity of the adsorption agent can be so small that it only amounts to a fraction of the quantities generally employed, contributes to the economy of the process. Because of the small demand upon the active carbon, moreover, the life of the laiter is almost unlimited.

A suitable apparatus for carrying out the process of the invention is shown diagrammati-

cally in the drawing:

Referring to the drawing a conduit 2 leads . from a gas holder I through a blower 3 to a cooler 4 which ecols the gas to a low tempera ture and which is connected through conduit 5 to an adsorption chamber 6 which contains active charcoal. There are provided at least two adscription chambers which are set in operation alternately, preferably bowever three, each of which is provided with devices for heating and cooling. Two conduits I and 8 branch off from each of the advorption chambers 6 connected ride by side. The conduit I hads to a gas holder 9, from which the gas collected is removed through the tube 10 whilst on the other hand the other conduit & leads to the suction side of a pump II, to the pressure side of which a condult 12 common to all the history on chambers is connected, which forks into the conduits 13 and 14. A two-way valve 15 is inserted at the forking place. The conduit 13 opens into the conduit 2 at a position in front of the blower 3 in the sense of the direction of flow. The conduit 14 leads to a gas holder 15, from which a compressor 18 sucks off the collected gas through the conduit 11 in order to send it through the conduit is into the converting plant 20. A pressure vessel 22 is connected into the lead-off 21 of the converting plant.

The plant works as follows: The starting mixture is suched out of the gas holder I by the blower 3 and pressed into the corder 6 in which it is cooled by way of example to -50° C. From here the mixture passes into an adsorption chamber 6, the charge of which is preceded to -50°C. During this process the valve I' in the conduit 7 is open and the valve 6' in the conduit 8 is cloved, so that the unbound mixture of carbon monchile and hydrogen escaping can flow through the conduit I to the gasometer 9 in which it is collected. The stream of starting mixture is now led into the eccond adsorption chamber and the first chamber is connected by closing the valve I' and opening the valve 3', with the pump If for the purpose of de-charging. Until a ceror physical subsequent purification methods. tain reduced pressure (for example 100 mms.) The portion of the desornate rich in cation 75 has been obtained a mixture is sucked off, the

carbon menoxide content of which is about equal carbon menoxide content of which is about equal to that of the starting mixture. This first running is led back through the conduit 13 into the starting mixture after the conduit 14 leading to the conversion plant has been closed by the two-way valve 15. Hereupon by turning the valve 15 the conduit 14 is opened to the gas alream and the pressure is continually further reduced until it : eaches a value of for example 10 mms. Thereby a gas injuture is driven out which contains to shoul 50% of carbon monoxide. This mixture passes through the conduit 14 into the gas holder 18, from which it is conveyed by the compressor 18 Into the conversion plant 20 where the carbon monoxide is removed by water gas oxidation to a 15 residual content of 3%. The purified gas after washing out the carbon dioxide passes out of the pressure vessel 22 through the conduit 21 to the place of use.

What I claim is:

1. A process for removing carbon monoxide from a mixture thereof with hydrogen which from a mixture thereof with hydrogen which comprises passing said inixture into confact with activated carbon at a temperature of the order of minus 50° C, and thereby selectively adsorbing carbon monoxide from the mixture at a high ratio, with respect to hydrogen, and thus producing an advantages, confeded in hydrogen, colducing an efficient gas enriched in hydrogen, collecting said efficient gas, and discentinuing passage of said mixture prior to the time when the 30 carbon monoxide content of the effuent gas increases suddenly.

2. A process for removing carbon moneraide from a minture thereof with hydrogen which comprises passing said mixture alternately in separate cycles through separate masses of activated calbon at a temperature of the order of minus 50° C, and in each such cycle thereby effecting selective adsorption of carbon monoxide from the minure at a high ratio, with respect to hydrogen, and thus producing an efficient gas enriched in hydrogen, collecting the chiuent gas, and discontinuing passage of the mixture to the mass in use and passing the mixture to the other mass just prior to the time when the carbon monoxide content of the chuent gas increases suddenly.

3. A process according to claim 2 in which the masses of activated carbon are subjected to reduced pressure, after discontinuing passage of said mixture, to thereby remove carbon monexide enriched adsorbate and condition the mass for

re-use.

4. A process according to claim 2 in which the masses of activated carbon are subjected to reduced pressure, after discontinuing passage said mixture, to thereby remove carbon monoxide enriched acsorbate and condition the mass for re-use, said pressure reduction being applied in stages and the first runnings comprising a fraction high in hydrogen being passed into the starting mixture.

KONRAD ERDMANN.

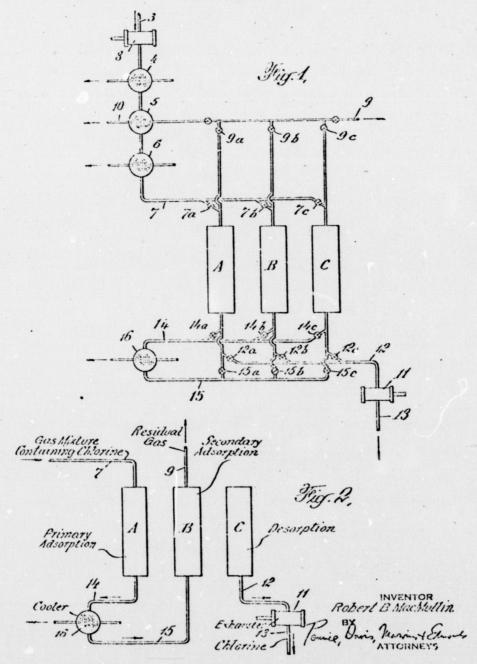
DEFENDANTS' EXHIBIT M(5)

14. MacMullin U.S. Patent No. 2,340,398

R. B. Mª MULLIN

CHEMICAL MANUFACTURE

Filed March 21, 1942





# UNITED STATES PATENT OFFICE

2,340,398

#### CHEMICAL MANUFACTURE

Robert B. MacMullin, Niagara Falls, N. Y., assignor to The Mathieson Alhali Works, Inc., New York, N. Y., a corporation of Virginia

Application March 21, 1942, Serial No. 435,643

4 Claims. (Cl. 183-114.2)

This invention relates to improvements in the separation and recovery of chlorine from gas mixtures containing chlorine. The invention relates particularly to improvements in separation and recovery operations in which chlorine is adsorbed from the gas mixture on silica gel and the adsorbed chlorine is then separated from the silica gel under a lower pressure than that prevailing during adsorption while the temperature level is maintained low enough to provide a useful margin of adsorptive capacity over the pressure differential uxed. The invention provides improvements in chlorine recovery and in an internally balanced cycle of operation.

In carrying out such operations, separate charges of the silica gel are successively used for adsorption of chlorine from the gas mixture and are then subjected to desorption to separate the recovered chlorine and to make the charge of gel again available for the adsorption step. The adsorption may be carried out in two or more stages by passing the gas mixture successively through two or more charges of gel advanced at regular intervals in countercurrent to the gas mixture and then subjected to desorption. During adsorption, the temperature of the charges of gel tends to rise due to the heat of adsorption and during description the temperature of the charges of gel tends to drop due to the best of vaporization of the chlorine. The effective adsorptive capacity of the silica gel, and consequently the recovery of chlorine, is limited by the temperature rise due to the heat of adsorption as well as by the adsorbed chlorine. To balance the cycle of such operations, 35 the quantity of chlorine removed in the adsorption step must correspond to that recovered in the description step and the net temperature increase of the gel during adsorption must cor-respond to the net temperature decrease of the gel during description. While refrigeration can be used to lower the general level of temperature of the operation, the low thermal conductivity of silica gel renders indirect heat exchange ineffective as a practical means of removing heat from a charge of gel. The present invention provides an internal thermal balance which is not impeded by the low conductivity of the silica gel and permits improved recovery of chlorine in such operations.

According to this invention, the gas mixture

According to this invention, the gas mixture containing chlorine is passed successively through silica gellin a primary adsorption step, then through a cooler, and then through silica gel in a secondary adsorption step. The gel 55 may be used, in indirect heat exchange, to cool

charged with adsorbed chlorine is transferred from the primary step to a desorption step in which chlorine is vaporized from the gel by reducing the pressure and the gel is cooled, by vaporization, substantially to a temperature at which the gel is transferred to the primary step. The gel partially charged with chlorine ac'sorbed in the secondary step is transferred to the primary step to replace that transferred to the desorption step. The gel from which chlorine has been separated in the desorption step is transterred to the secondary step to replace that transferred to the primary step. The gas mixture passing from the primary step to the sec-ondary step is cooled, in the cooler previously mentioned, sufficiently to maintain the temperature of the gel transferred from the secondary step to the primary step substantially that of the gel transferred from the desorption step to the secondary step. An improved recovery of enforme is effected in this secondary adsorption step. Also, the cycle of operation is internally balanced, making the operation truly cyclic, in a manner which eliminates the low thermal conductivity of the silica gel as an impediment to the heat exchanges involved. Heat exchanges within the charges of gel are effected, in accordance with this invention, by the adsorption of chlorine, by the vaporization of chlorine, and by 30 the gas mixture itself passing through the get.
All thermal factors with respect to which the distribution of the heat exchange medium and me heat to be absorbed are linerated are substantially coextensive except for the cooling of the ges mixture passing from the primary adsorption step to the secondary adsorption step. The cooling of the gas mixture at this point by conventional indirect heat exchange involves no technical dimenties and does not involve the low conductivity of the silica get. The operation is with advantage carried out with a series of separate charges of silica gel which are at regular intervals transferred as such from the desorption step to the secondary adsorption step, then to the primary adsorption step and then back to the desorption step, each charge of gel leaving the desorption step at a temperature corresponding to the initial temperature of the charge at the beginning of each primary adsorption step in the cycle and passing through the recondary adsorption step without substantial change in temperature. The residual gas the gas mixture supplied to the primary adsorption step.

The invention will be further described in connection with the accompanying drawing which illustrates, diagrammatically and conventionally, one embediment of the practice of the invention. In the drawing, Fig. 1 illustrates apparatus for carrying out the cycle of operation constituting the invention and Fig. 2, as a flow diagram, illustrates one of the cyclically repeat- 10

ed stages of operation.

Referring to the drawing: the cillorine-containing gas mixture supplied through connection \$ is forced through coolers 6, 5 and 6, connection 7 and two of the three absorbers A, B and C charged with silica gel by means of compressor 8. After passing through the second absorber, the residual gas mixture is either discharged through connection 6 or through cooler 6 and connection 16. The cooler 4 may be supplied 20 with cooling water and the cooler 6 may be supplied with chilled brine or other appropriate refrigerant, for example. The adsorbed chlorine is vaporized from one of the three absorbers A. B and C by means of exhauster 11 through con-nection 12, the recovered chlorine being discharged through connection 13. After leaving the first of the two absorbers through which it passes and before entering the second, the eas mixture supplied through connection 1 passes, by means of connections 14 and 16, through cooler 16. The cooler 16 may be supplied with chilled brine or other appropriate refrigerant, for example. The several connections 7, 14, 15, and -10 are manifolded to the three absorbers to 35 permit the transfer, stage by stage as the cycle of operation proceeds, of the charge of silica gel in each absorber to the next step of the operation. The compressor 8 and the exhauster 11 may each be compounded and provided with intercoolers as 40 in conventional practice. If the concentration with respect to chlorine of the gas mixture supplied through connection 3 is so high that con-densation of chlorine occurs during passage through the coolers 4, 5 and 6, provision may be made for separation of condensed chlorine from the gas mixture before the gas mixture reaches the absorbers. The several absorbers A, B and C may be thermally insulated and may be provided with refrigerated jackets to reduce the general 50 temperature level at which the operation is carried out.

In initiating operation in the illustrated equipment, for example, the valves 1a, 8b, 14a, 15b and 12c are opened and the valves 1b, 1c, 8a, 8c, 14b, 14c, 15a, 15c, 12a and 12h are closed. The operating situation of the absorbers A, B and C will then be as illustrated in Fig. 2. In this situation, the chlorine-contining gas miriture may be supplied to absorber A under a pressure of from 2 to 10 atmospheres and may be discharged from absorber B at a pressure corresponding with the supply pressure and the pressure differential due to the flow through the absorbers A and B and the cooler 16. The absorber C may be brought, dur-ing desorption, to a pressure of from 0.1 atmosphere to about 1 atmosphere, for example. As the adsorption of chlorine by the charge of silica gel in absorber A proceeds, the temperature of this charge of gel rises from a temperature Ti 70 to a temperature Ts. As a consequence of the desorption, the temperature of the charge of sel in absorber C is brought from the temperature

the gas mixture leaving absorber A, but in this secondary adsorption step the mean temperature of the charge of gel is maintained substantially at Ti by cooling, in the cooler 16, the gas mixture leaving the absorber A before it enters the absorber B to a temperature To such that the recidual gas mixture leaving the absorber B will carry away sufficient heat to maintain this temperature. When the charge of gel in absorber A reaches a temperature of To and the charge of gel in absorber B reaches a temperature of Ti. valves 1a, 9b, 14a, 16b and 12c are closed and valves 1b, 9c, 14b, 15c and 12a are opened and the operation is repeated, the charge of gel in the absorber A being brought to a temperature of Ti and the charge of gel in absorber B being brought to a temperature of To while the charge of gel in the absorber C is maintained at a temperature of Ti in this stage. In the stage of operation first described, the primary adsorption is carried out in absorber A, the secondary adsorption in absorber E and the descrption in absorber C, and in the second stage of operation the primary adsorption is carried out in absorber B, the secondary adsorption in absorber C and the desorption in absorber A, the change in position of the control valves between the first and second stages amounting to a transfer of the charge of gel from the description step to the secondary adsorption step, from the secondary adsorption step to the primary adsorption step and from the primary adsorption step to the desorption step. In the third stage of operation, the primary adsorption is carried out in absorber C, the secondary adsorption in absorber A and the desorption in absorber B, and the succeeding stages of operation continue in the same manner. The general temperature level at which the operation is carried out may be fixed by fixing the temperature T<sub>4</sub> at which the chlorine-containing gas mixture is supplied to the primary adsorption step, or by controlling this temperature Te and the temperature of the environment of the several absorbers, for example by refrigerated jackets. This temperature Te is controlled so that the temperature rise in the primary adsorption step equals the temperature fall in the desorption step.

The several temperatures just designated Ti, T2, T3 and T4 may vary considerably in varying applications of the invention, particularly with varying concentrations of chlorine in the gas mixture from which it is to be separated and recovered. In general, the initial temperature of the charge of sel in the primary adsorption to be such as with advantage not higher than shout 10° step is with advantage not higher than about 10° C., or better 0° C. or lower, this being the temperature previously designated Ti. The temperature to which the gas mixture is cooled between the primary adsorption step and the secondary adsorption step, the temperature previously desgnated To is lower than this initial temperature. The final temperature to which the charge of gel is brought in the primary adsorption may be as high as 35°-40" C., or even higher, any chlorine escaping unadsorped at this temperature being separated from the gas mixture in the secondary adsorption. As applied to the separation and recovery of chlorine from gas mixtures containing from about 10% to about 35% (by volume) chiorine, for example, the temperature Ti may approximate -20° C. -25° C., for example, the temperature T2 may approximate 25° C., 40° C., To the temperature Ti. The charge of gel in for example, the temperature Ti may approxi-absorper B is separating additional chlorine from 75 mate -25° C., -37° C., for example, and the

temperature Te may approximate -10° C., -25° C., for example, with working pressures renging from 10 atmospheres in the primary adsorption step to 0.1 atmosphere in the desorption step.

The chlorine recovered from the desorption step may, for example, he liqueded in any con-ventional manner. The process of this invention is applicable to gas intitures containing chlorine in concentrations ranging from as little as 10% or less to as much as 50% and more, even to 10 concentrations of the order of 80%. As applied to gas mixtures containing chlorine in low concontration, the invention is particularly advan-tageous because of the high recoveries it provides. As applied to gas mixtures containing 15 chloring in high concentration, the invention is particularly adventageous because of the balanced cycle of operation it provides notwithstanding the substantial heat exchanges lavolved as a consequence of the high heat of adscription of go chlorine on silica gel

1. In the recovery of chlorine from gas micetures containing the cause, the improvement which comprises passing the gas mixture successively through silica gel in a primary adsorption step, a cooler, and silica gel in a secondary adsorption step, transferring gel charged with chlorine from the primary step to a desorption step, vaporizing chlorine from the gel in the description so step by reducing the pressure and thereby cooling the gel substantially to the temperature at which the gel is transferred to the primary step, transferring gel partially charged with chlorine from the secondary step to the primary step to 35 temperature fall in the description step. replace that transferred to the description step. transferring gel from the description step to the

commdary step to replace that transferred to the primary step, and cooling the gas miniture passing from the primary step to the seconds / step sufficiently to maintain the temperature of the gel transferred from the recondary step to the primary step substantially that of the gel transferred from the description step to the secondary

2. In the recovery of chlorine from gas mix-tures cont-ining the same, the improvement which comprises subjecting the gas mixture to a first treatment with a first charge of silica gel at a temperature increasing from an initial temperature to a higher temperature, cooling the gas mixture from that treatment and subjecting it to a second treatment with a second charge of silica gel at a temperature approximating said initial temperature, subjecting a third charge of gel to description by reducing the pressure and thereby cooling the gel to said initial temperature, transferring the second charge of gel to the first treatment, transferring the filled charge to the second treatment and transferring the first charge to the description.

3. In the process of claim 1, the improvement which comprises possing the gas minture from the secondary adsorption step in indirect heat exchange with the ges mixture supplied to the

primary adsorption step.
4. In the process of claim 1, the improvement which comprises controlling the temperature at which the chlorine-containing gas mixture is supplied to the primary adsorption step so that the temperature rise in that step equals the

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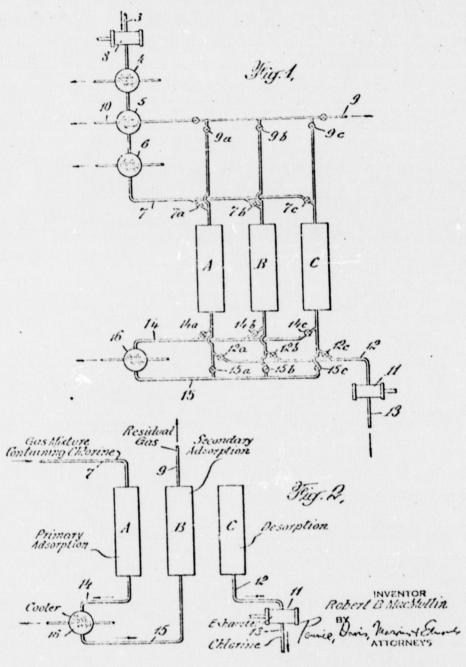
DEFENDANTS' EXHIBIT M(5)

15¢ Dailey U.S. Patent No. 2,535,902

R. B. Mª MULLIN

CHEMICAL MANUFACTURE

Filed March 21, 1942





# UNITED STATES PATENT OFFICE

2,340,398

### CHEMICAL MANUFACTURE

Robert B. MacMullin, Niagara Falls, N. Y., assignor to The Mathieson Alhali Works, Inc., New York, N. Y., a corporation of Virginia

Application March 21, 1942, Serial No. 435,643

4 Claims. (Cl. 183-114.2)

This invention relates to improvements in the separation and recovery of chlorine from gas mixtures containing chlorine. The invention relates particularly to improvements in separation and recovery operations in which chlorine is adsorbed from the gas mixture on silica gel and the adsorbed chlorine is then separated from the silica gel under a lower pressure than that prevailing during adsorption while the temperature level is maintained low enough to provide a useful margin of adsorptive capacity over the pressure differential uccd. The invention provides improvements in chlorine recovery and in an internally balanced cycle of operation.

In carrying out such operations, reparate charges of the silica gel are successively used for adsorption of chlorine from the gas mixture and are then subjected to desorption to separate the recovered chlorine and to make the charge of gel again available for the adsorption The adsorption may be carried out in two or more stages by passing the gas mixture successively through two or more charges of gel advanced at regular intervals in countercurrent to the gas mixture and then subjected to de-sorption. During adsorption, the temperature of the charges of gel tends to rise due to the heat of adsorption and during descrption the temperature of the charges of gel tends to drop due to the heat of vaporization of the chlorine. The effective adsorptive capacity of the silica gel, and consequently the recovery of chicrine, is limited by the temperature rise due to the heat of adsorption as well as by the adsorbed chlorine. To balance the cycle of such operations, the quantity of chlorine removed in the adsorption step must correspond to that recovered in the desorption step and the net temperature increase of the gel during adsorption must cor-respond to the net temperature decrease of the gel during description. While refrigeration can be used to lower the general level of temperature of the operation, the low thermal conduc-tivity of silica gel renders indirect heat exchange ineffective as a practical means of removing heat from a charge of gel. The present invention provides an internal thermal balance which is not impeded by the low conductivity of the silica and permits improved recovery of chloring in such operations.

According to this invention, the gas mixture containing chlorize is passed successively through silica gellin a primary adsorption step, then through a cooler, and then through silica gel in a secondary adsorption step. The gel 65 may be used, in indirect heat exchange, to cool

charged with adsorbed chlorine is transferred from the primary step to a desorption step in which chlorine is vaporized from the gel by reducing the pressure and the gel is cooled, by vaporization, substantially to a temperature at which the gel is transferred to the primary step. The gel partially charged with chlorine acsorbed in the secondary step is transferred to the pri-mary step to replace that transferred to the desorption step. The gel from which chlorine has been separated in the desorption step is transferred to the secondary step to replace that transferred to the primary step. The gas mix-ture passing from the primary step to the secondary step is cooled, in the cooler previously mentioned, sufficiently to maintain the temperature of the gel transferred from the secondary step to the primary step substantially that of the gel transferred from the desorption step to the secondary step. An improved recovery of enforme is effected in this secondary adsorption step. Also, the cycle of operation is internally balanced, making the operation truly cyclic, in a manner which chimmates the low thermal conductivity of the silica gel as an impediment to the heat exchanges involved. Heat exchanges within the charges of gel are effected, in accordance with this invention, by the adsorption of chlorine, by the vaporization of chlorine, and by the gas mixture liself passing through the get All thermal factors with respect to which the distribution of the heat exchange medium and ne heat to be absorbed are liberated are substantially coextensive except for the cooling of the ges mixture passing from the primary adsorption step to the secondary adsorption step. The cooling of the gas mixture at this point by conventional indirect heat exchange involves no technical amounties and does not involve the low conductivity of the silica get. The operation is with advantage carried out with a series of separate enarges of silica gel which are at regular intervals transferred as such from the desorption step to the secondary adsorption step, then to the primary adsorption step and then back to the description step, each charge of gel leaving the desorption step at a temperature corresponding to the initial temperature of the charge at the beginning of each primary adsorption step in the cycle and passing through the accordary adsorption step without substantial change in temperature. The residual gas the gas mixture supplied to the primary adsorptien step.

The invention will be further described in connection with the accompanying drawing which illustrates, diagrammatically and con-ventionally, one embediment of the practice of the invention. In the drawing, Fig. 1 illustrates apparatus for carrying out the cycle of operation constituting the invention and Fig. 2, as a flow diagram, illustrates one of the cyclically repeat-

ed stages of operation.

Referring to the drawing: the colorine-containing gas mixture supplied through connection is forced through coolers 4, 5 and 6, connection and two of the three absorbers A, B and C charged with silica gel by means of compressor After passing through the second absorber, the residual gas mixture is either discharged through connection \$ or through cooler 6 and connection 16. The cooler 4 may be supplied with cooling water and the cooler & may be supplied with chilled brine or other appropriate refrigerant, for example. The adsorbed chiorine is vaporized from one of the three absorbers A. B and C by means of exhauster 11 through connection 12, the recovered chlorine being discharged through connection 13. After leaving the first of the two absorbers through which it passes and before entering the second, the cas mixture supplied through connection 7 passes, by means of connections 14 and 15, through cooler 16. The cooler 16 may be supplied with chilled brine or other appropriate refrigerant, for example. The several connections 7, 14, 15, and -10 are manifolded to the three absorbers to 35 permit the transfer, stage by stage as the cycle of operation proceeds, of the charge of silica gel in each absorber to the next step of the operation. The compressor 8 and the exhauster 11 may each be compounded and provided with intercoolers as conventional practice. If the concentration with respect to chlorine of the gas mixture supplied through connection \$ is so high that condensation of chlorine occurs during passage through the coolers 4, 5 and 6, provision may be made for separation of condensed chlorine from the gas mixture before the gas mixture reaches the absorbers. The several absorbers A, B and C may be thermally insulated and may be provided ried out.

In initiating operation in the illustrated equip ment, for example, the valves 1a, 8b, 14a, 16b and 12c are opened and the valves 1b, 1c, \$a, \$c, 14b, 14c, 15a, 15c, 12a and 12b are closed. The operating situation of the absorbers A, B and C will then be as illustrated in Fig. 2. In this situation, the chlorine-contining gas mixture may be supplied to absorber A under a pressure of from 2 to 10 atmospheres and may be discharged from absorber B at a pressure corresponding with the supply pressure and the pressure differential due to the flow through the absorbers A and B and the cooler 16. The absorber C may be brought, during desorption, to a pressure of from 0.1 atmosphere to about 1 atmosphere, for example. the adsorption of chlorine by the charge of silica gel in absorber A proceeds, the temperature of this charge of gel rises from a temperature Ti 70 to a temperature T2. As a consequence of the desorption, the temperature of the charge of sel in absorber C is brought from the temperature T2 to the temperature T1. The charge of gel in

the gas mixture leaving absorber A, but in this secondary adsorption step the mean temperature of the charge of gel is maintained substantially at Ti by cooling, in the cooler if, the gas mixture leaving the absorber A before it enters the absorber B to a temperature To such that the recidual gas mixture leaving the absorber B will carry away sufficient heat to maintain this temperature. When the charge of gel in absorber A 16 reaches a temperature of T; and the charge of gel in absorber B reaches a temperature of Ti. valves 1a, 9b, 16a, 16b and 12c are closed and valves 1b, 9c, 14b, 16c and 12a are opened and the operation is repeated, the charge of gel in the absorber A being brought to a temperature of Ti and the charge of gel in absorber B being brought to a temperature of T2 while the charge of gel in the absorber C is maintained at a temperature of Ti in this stage. In the stage of operation first described, the primary adsorption is carried out in absorber A, the secondary adsorption in absorber E and the description in absorber C, and in the second stage of operation the primary adsorption is carried out in absorber B, the secondary adsorption in absorber C and the desorption in absorber A, the change in position of the control valves between the first and second stages amounting to a transfer of the charge of gel from the description step to the secondary adsorption step, from the secondary adsorption step to the primary adsorption step and from the primary adsorption step to the desorption step. In the third stage of operation, the primary adsorption is carried out in absorber C, the secondary adsorption in absorber A and the desorption in absorber B, and the succeeding stages of operation continue in the same manner. The general temperature level at which the operation is carried out may be fixed by fixing the temperature Te at which the chlorine-containing gas mixture is supplied to the primary adsorption step, or by controlling this temperature Te and the temperature of the environment of the several absorbers, for example by refrigerated jack-This temperature To is controlled so that the temperature rise in the primary adsorption step equals the temperature fail in the desorption step.

The several temperatures just designated Ti, with refrigerated jackets to reduce the general 50 T2, T3 and T4 may vary considerably in varying temperature level at which the operation is carvarying concentrations of chlorine in the gas mixture from which it is to be separated and recovered. In general, the initial temperature of the charge of gel in the primary adsorption step is with advantage not higher than about 10° C., or better 0° C. or lower, this being the temperature previously designated Ti. The temperature to which the gas mixture is cooled between the primary adsorption step and the secondary adsorption step, the temperature previously designated To is lower than this initial temperature. The final temperature to which the charge of gel is brought in the primary adsorption may be as high as 35°-40" C., or even higher, any colorine escaping unadsorbed at this temperature being separated from the gas mixture in the secondary adsorption. As applied to the separation and recovery of chlorine from gas mixtures containing from about 10% to about 35% (by volume) chiorine, for example, the temperature Ti may opproximate -20° C., --25° C., for example, the temperature T<sub>2</sub> may approximate 25° C., 40° C., To the temperature Ti. The charge of gel in for example, the temperature Ti may approxi-absorber B is separating additional chlorine from 75 mate -25° C., -37° C., for example, and the

temperature Te may approximate -10° C., -25° C., for example, with working pressures renging from 10 atmospheres in the primary adtorption step to 0.1 atmosphere in the descrition step.

The chlorine recovered from the desorption step may, for example, he liqueded in any con-ventional manner. The process of this invention is applicable to gas mixtures containing chlorine in concentrations ranging from as little as 10% or less to as much as 50% and more, even to 10 concentrations of the order of 50%. As applied to cas mixtures containing chlorine in low concentration, the invention is particularly advantageous because of the high recoveries it provides. As applied to ges mixtures containing 15 chlorine in high concentration, the invention is particularly adventageous because of the balanced cycle of operation it provides notwithstanding the substantial heat exchanges involved as a consequence of the high heat of adscription of 20 chlorine on silica gel

I claim:

1. In the recovery of chiorine from gas mixtures containing the cause, the improvement which comprises passing the gas mixture successively through silies sel in a primary adsorption step, a cooler, and silies sel in a secondary adsorption step, transferring gel charged with chlorine from the primary step to a description step, vaporizing chlorine from the gel in the description as step by reducing the pressure and thereby cooling the gel substantially to the temperature at which the gel is transferred to the primary step, transferring gel partially charged with chlorine from the secondary step to the primary step to 25 temperature fall in the description step. transferring gel from the description step to the

secondary step to replace that transferred to the primary step, and cooling the gas miniture passing from the primary step to the sucendary step sufficiently to maintain the temperature of the gel transferred from the recondary step to the primary step substantially that of the gel transferred from the description step to the secondary

2. In the recovery of chlorine from gas mixtures containing the same, the improvement which comprises subjecting the gas minture to a first treatment with a first charge of cilics gel at a temperature increasing from an initial tempecature to a higher temperature, cooling the gas mixture from that treatment and subjecting it to a second treatment with a second charge of silica gel at a temperature approximating said initial temperature, subjecting a third charge of gel to desorption by reducing the pressure and thereby cooling the gel to said initial temperature, transferring the second charge of gel to the first treatment, transferring the filled charge to the second treatment and transferring the first charge to the description.

3. In the process of claim 1, the improvement which comprises possing the gas minture from the secondary adsorption step in indirect heat exchange with the gos mixture supplied to the

primary adsorption step.
4. In the process of claim 1, the improvement which comprises controlling the temperature at which the chlorine-containing gas mixture is supplied to the primary adsorption step so that the temperature rise in that step equals the

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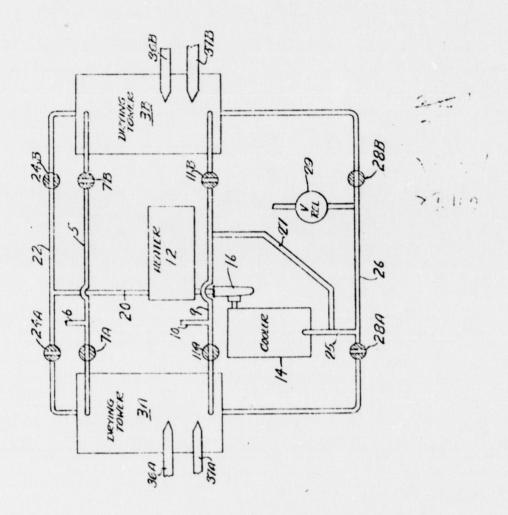
DEFENDANTS' EXHIBIT M(5)

15. Dailey U.S. Patent No. 2,535,902

W. H. DAILEY, JR

GAS DRIER

Filed March 7, 1947



William H. Dailey Jr.

2004 Double & Dakton

His attorney



# UNITED STATES PATENT OFFICE

GAS DRIER

William H. Dailey, Jr., Library, Pa., assigner to Carnegle-Illinois Steel Corporation, a corporation of New Jersey

Application March 7, 1947, Serial No. 733,019

6 Claims. (Cl. 183-4.5)

This invention relates to gas dryers and more particularly to such gas dryers as are used to dry the gases used for protective atmospheres in the annealing of steel, although not limited

In the annealing of steel the gases which are used for protective atmospheres are usually of such a nature that they require more or less complete drying before being used. When the protective atmosphere comprises nitrogen gas, or nitrogen containing small percentages of deoxidizing gases such as carbon monoxide or hydrogen, it is particularly important that there be a very low water vapor content. It has been frigeration, thus condensing out water vapor; or by using desiccants such as activated alumina, silica jell, etc. Frequently desiccants are used following refrigeration.

property of adsorbing water vapor onto their surfaces in quantities up to 5 to 15% of their weight. The residual water vapor content of the gas to be dried may be reduced to 0.01% or less, quantity of incoming moisture, and other factors.

It is customary to employ two containers or adsorber towers containing the desiccant, and to operate one tower while the other is disconnected and subjected to heat in order to drive off the 30 water vapor. After the water vapor is driven off, the desiceant is cooled to a temperature sufficiently low to permit satisfateory operation and is then ready to dry additional gases.

Drying equipment of the type described is not 35 entirely satisfactory due to the difficulty in heating and cooling the desiccant. It is usually the practice to embed heating and cooling coils in the charge of desiceant. The heating means may be steam, electricity, etc. In other cases, the desiccant is heated by blowing hot air or hot combustion gases through it. Cooling is accom-plished by coils embedded in the desiccant, or, by external cooling coils through which air or other gas is circulated. The principal objection to 45 these systems is the length of time that is required for reactivating, contamination due to air or combustion gases, and the difficulty in maintaining the embedded heating and cooling surfaces.

It is among the objects of the present inven- 50 tion to provide an improved gas dryer which is not possessed of the shortcomings of the prior art, as recited hereinbefore.

Another object is to provide a completely closed system of to class described, together 65 with means for pre enting the entry of air or other contaminating gas.

The foregoing and other objects will become more apparent after referring to the accompanying specification and drawing, in the latter of which:

The drawing is a flow diagram illustrating an arrangement of equipment suitable for carrying out the methods of the present invention.

Referring more particularly to the drawing, the apparatus of the invention takes the form of a unit comprising a frame, not shown, on which there is mounted a pair of vertically extending desiceant containers or drying towers 3A and 3B which are disposed in adjacent relationship and constructed and arranged for easy access to the customary to dry these gases by means of re- 15 interiorly disposed desiceant. A gas inlet manifold 5 extends horizontally between and connects the upper ends of the drying towers 3A and 2B, the said manifold being provided with a gas inlet pipe 6 and valves 7A and 1B located at either Desiceants of the type described possess the 20 side of the pipe 6. A dry gas outlet manifold \$ extends horizontally between, and connects the lower ends of the drying towers 3A and 3B, valves 11A and 11B being provided for disconnecting said towers and a gas outlet pipe 10 being condepending upon the particular desiccant, the 25 nected to the gas outlet manifold at a point which lies between the said valves IIA and IIB.

The above arrangement is conventional. permits one tower to be placed in drying service and when the desiccant in this tower becomes saturated shifting to a second tower, thus uninterrupted drying service is obtained. The saturated desiccant in the first tower is reactivated during the time the second tower is in drying service.

The unit of the present invention includes an improved reactivating system including an ex-

ternal convection heater 12 and an external convection cooler 14 through both of which gas may be circulated as by means of the pump or blower 16 which is shown as being intermediately disposed. The heater 12 and cooler 14 may be combined as a single heat transfer surface, or they may take the form of separate units, as

shown, which I prefer.
The towers 3A and 3B are connected to the outlet side of the heater 12 through a pipe 20 and a common header 22. Located in the header 22 and on either side of the pipe 20 are disconnect valves 24A and 24B. The towers are connected to the inlet of the cooler 14 through a pipe 25 and a common return header 26. Disconnect valves 28A and 28B are provided in the header 26 on either side of the pipe 25. Pipe 21 of relatively small bore connects the dry gas manifold 9 to the inlet side of the cooler 14. The pipe 21 can be termed a purge line which supplies fresh dry gas to the reactivating system. A 2,585,902

pressure relief valve 28 is provided in the return header 26 between the valves 28A and 28B. The relief valve 29 exhausts to the atmosphere and is set to open at a pressure above atmospheric but below the pressure of the dry gas supplied from the heater 9 through the purge line 21. In this manner the water removed from the desiccant is gradually expelled from the reactivating system. An orifice plate can be substituted for the relief valve 29 if desired.

The normal cycle of operation is as follows: The deoxidizing gas enters the drying apparatus through the common inlet connection 6 and is directed into one or the other of the drying towers. In Figure 1 valve IB is shown closed and valve 1A is shown open; the gas to be dried is, therefore, directed into tower 3A. The gas then passes downward through the desiccant bed where the water vapor content is absorbed and leaves the tower at the bottom from where it is directed into the common outlet connection 10, valve IIA being open and IIB closed. Normal operating procedure is to use one tower for dry-ing while the other tower is being reactivated, thus insuring a constant flow of dry gas to the 25

annealing furnaces.

When the desiccant in tower 3A becomes saturated, a suitable procedure for the operation of the hereinbefore described apparatus is to close the gas inlet and outlet valves, 7A and 11A, and open valves 1B and 113, thus bringing tower 3B into drying service. At the same time valves 24B and 28B are closed and valves 24A and 28A are opened which will cause the gas remaining in tower 3A to be circulated through desiccant con- 35 tainer of tower SA and the heat exchangers (12-14) by means of the blower 16. The heat exchanger 12 is controlled to heat the gas to some maximum temperature, usually 600° F., when activated alumina is used as the desiccant. The hot gas heats the desiccant. As the temperature of the desiccant approaches 200° F., water vapor is given off in very large quantities, almost proportional to the amount of heat applied, so that a mixture of steam and gas leaves the tower 3A at the bottom thereof through header 26

A portion of this mixture is bled off through the relief valve 29 and is replaced by fresh dry gas from the header 9 through the purge line 21. The steam is, therefore, gradually replaced with dry gas from the purging inlet connection. As 50 the drying of the desiccant proceeds the temperature of the gas leaving the tower rises. When the gas leaving the alumina reaches a predetermined temperature of, for example, 550° F. (indicating that all of the desiceant has approached 65 or exceeded this temperature), the drying is substantially complete and the heat is turned off and cooling is started, as by turning water into the cooler 14. Cooling is continued until the gas leaving the desiceant reaches a temperature low co enough to insure efficient adsorption of the water vapor. For activated alumina, this temperature is 80 to 100 F. When this temperature is attained, tower 3A is ready for drying service, and tower 3B can be removed from drying service and 65 its desiceant reactivated. Means for measuring the temperature of the gas in the pipes 20 and 25 are provided; such means are well known to the art and have not, therefore, been shown.

The above mode of operation is necessary when 70 the heater 12 and the cooler 14 are combined in a single unit, however, as previously stated, I prefer to use separate heat transfer units for cooling and heating as this permits water or

through the cooling heat exchanger, and additional steam to be removed by condensation in This will allow a somewhat greater the cooler. rate of reactivation, since the fan or blower 16 would be operating at a low temperature and is able to circulate a greater mass of drier gas. The heat required for reactivation is not greatly increased by this modification since during the major portion of the reactivating time the majority of the heat imparted to the gas by the heater 12 is used in vaporizing water from the desiccant, i. e., the gas which enters the tower at about 600° F. leaves at about 200 to 250°

The system thus far described, including the modification thereof, is a single stage system insofar as the desiccant is concerned and requires that the temperature of the entering wet gas be low enough so that the entering temperature plus the rise in temperature due to condensation of moisture on the desiccant does not exceed the effective operating temperature of the desiccant as a moisture absorbent.

The entering temperature of the wet gas is commonly reduced to an acceptable value by the use of a conventional refrigerating machine which, as such, forms no part of the present invention and accordingly is neither shown nor described.

When using the apparatus of the prior art, it is extremely difficult to determine when the desiceant is approaching saturation, since usually the moisture content of the exit gas remains at an extremely low value until saturation of the desiceant occurs, and then rises very rapidly. The teachings of the present invention contemplate the control of the time in drying service by means of conventional temperaturemeasuring devices which are located at various levels in the desiccant to detect the level at which maximum adsorption occurs by measuring the temperature difference between the said levels. For example, thermocouples 36A and 37A, and 36B and 37B or other temperature-measuring devices may be embedded in the desiccant at two different levels near the exit end of the towers 3A and 3B, respectively. The thermocouples 36A and 37A (or 36B and 37B when tower \$B is in drying service) will read substantially the same until the zone of maximum adsorption passes the first of the two or thermocouple 36A. At this time, its temperature will drop, while that of the thermocouple 37A which is nearer the exit of tower 3A remain at a higher temperature, thus indicating that the zone of adsorption is between the two and near the exit end of the tower A.

In addition, it is also proposed to automatically turn off the heater 12 during reactivation (when the exit gas reaches the desired temperature), turn on the cooling water, and automatically switch the inlet, outlet and recirculating valves when the adsorption zone reaches a predetermined level in the drying tower by means of these couples and conventional control equipment not shown.

While I have shown and described certain specific embodiments of my invention, it will be understood that these embodiments are merely for the purpose of illustration and description and that various other forms may be devised within the scope of my invention, as defined in the appended claims.

I claim:

1. The method of providing a continuous supply of dry gas wherein at least two containers of desiceant are used, which method comprises pastother cooling medium to continuously flow 75 ing the wet gas through a container of active 2,506,002

F. desiccant while reactivating a second container of moisture saturated desiccant, said reactivating step including heating a portion of the gas to a temperature sufficient to vaporize moisture in the saturated desiceant, forethly circulating said 5 heated gas through the moisture saturated desiccant to vaporize said moisture, gradually purging said circulating gas of vaporized moisture by continually bleeding-off a portion of the gas after it leaves the container of desiceant being reactivated and replacing said bled-off portion with dry gas issuing from the container of active desiceant; said heating, forced circulation and purging being continued until substantially all moisture is removed from the desiceant being reac- 15 tivated, and then cooling the reactivated desiceant to its operating temperature by continuing the forced circulation and purging while cooling the

circulating gas 2. The method of providing a continuous supply 20 of dry gas wherein at least two containers of alumina are used, which method comprises passing the wet gas through a container of active alumina while reactivating a second container of moisture saturated alumina, said reactivating step 25 including heating a portion of the gas to a temperature of about 600° F., fercibly circulating said heated gas through the moisture saturated alumina to vaporize said moisture, gradually purging said circulating gas of vaporized moisture by continually bleeding-off a portion of the gas after it leaves the container of alumina Leing reactivated and replacing said bled-off portion with dry gas issuing from the container of active alumina; said heating, forced circulation and purging being 25 continued until the temperature of the gas leaving the container of alumina being reactivated approaches the temperature of the gas entering said container, and then cooling the reactivated alumina to a temperature of about 100° F. by continuing the forced circulation and purging while cooling the circulating gas.

The method of providing a continuous supply of dry gas wherein at least two containers of desiccant are used, which method comprises passing the wet gas through a container of active desiceant while reactivating a second container of moisture saturated desiccant, said reactivating step including heating a portion of the gas to a temperature sufficient to vaporize moisture in the saturated desiceant, forcibly circulating said heated gas through said moisture saturated desiceant to vaporize said moisture, bleeding-off a portion of the moisture containing gas after it leaves the container of desiceent being re-activated and replacing said bled-off portion with dry gas issuing from the container of active desiceant whereby the vaporized moisture is gradually purged from the circulating gas, cooling the circulating gas to further lower its moisture content; said heating, forced circulation, purging and cooling being continued until substantially all moisture is removed from the desiccant being reactivated and then discontinuing the heating but continuing the forced circulation, purging and cooling until the temperature of the reactivated desiccant is lowered to its operating temperature.

6 4. The method of providing a continuous supply of dry gas wherein at least two containers of alumina are used, which method comprises passing the wet gas through a container of active alumina while reactivating a second container of moisture saturated alumina, said reactivating step including heating a portion of the gas to a temperature of about 600° F., foreibly circulating said heated has through said moisture saturated 10 alumina to vaporize said moisture, bleeding-off a portion of the moisture containing gas after it leaves the container of alumina being reactivated and replacing said bled-off portion with dry cas issuing from the container of active alumina whereby the vaporized moisture is gradually purged from the circulating gas, cooling the circulating gas to further lower its moisture content; said heating, forced circulation, purging and cooling being continued until the temperature of the gas leaving the container of alumina being reactivated approaches the temperature of the gas entering said container, and then discontinuing the heating but continuing the forced circulation, purging and cooling until the temperature of the reactivated alumina is lowered to about 100° F.

5. Apparatus for providing a continuous supply of dry gas comprising at least two containers of desiccant, a wet gas main, a dry gas main, a heat exchanger, a blower connected in series flow relationship with said heat exchanger, means for selectively connecting said containers to said gas mains, means for selectively connecting said containers to said heat exchanger and blower, means connected to said last named connecting means for bleeding-off moisture containing gas, and means connected to the last named connecting means for replacing said bled-off gas with dry gas.

6. Apparatus for providing a continuous supply of dry gas comprising at least two containers of desiccant, a wet gas main, a dry gas main, a heat exchanger unit adapted to heat gas, a blower, a heat exchanger unit adapted to cool gas, said heater, blower and cooler units being connected in series flow relationship, means for selectively connecting said containers to said gas mains, means for selectively connecting said containers to said heater, blower and cooler units, means connected to said last named connecting means for bleeding-off moisture containing gas, and means connected to the last named connecting means for replacing said bled-off gas with dry gas.

#### WILLLIAM H. DAILEY, JR.

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# DEFENDANTS' EXHIBIT M(5)

19. Kahle German Patent No. 871,886 and Translation

(Thanked on the frame of the hill hanke four of fully 8, 1949)

Erreilt auf Grund des Ersten Überleitungsgesetzes vom 8. Juli 1949

BUNDESRÉPUBLIK DEUTSCHLAND

Chand in Mickey ( 11.5)

AUSGEGEBEN AM 26. MXRZ 1953



PATENTS CHRIFT

Nr. 871 886

KLASSE 12e GRUPPE 302 (class) G.105 IV b/ 120 (July)

Dipl.-Chem. Dr. Fing. Heinrich Kahle, Pullach bei München ist als Erfinder genannt worden (is named as inventer)

### Gesellschaft für Linde's Eismaschinen A.-G., Höllriegelskreuth bei München (addreption - Process)

Adsorptionsverfahren

Der Zeitraum vom 8. Mai 1945 bis einschließigen 7. Mai 1950 wird auf die Patentauer nicht angerechnet

Patentaum vom 8. Mai 1945 bis einschließigen 7. Mai 1950 wird auf die Patentauer nicht angerechnet

Patentaum eldung bekanntigemacht au 27. September 1951

Patenterteilung bekanntigemacht am 19. Februar 1953

Es ist bekannt, zur Entiernung oder Gewinnung von Mischungsbestandteilen aus Gasgemischen Adsorptionsverfahren anzuwenden und mit Adsorptionsmitteln gefüllte Behälter, die sogenannten Ad-5 sorber, paarweise anzuordnen, welche zum Zweck der Ausorption und Desorption periodisch umgeschaltet werden. Bei der Desorption durch Spülung mittels eines Gases oder durch Evakuierung wird das Gas in der Regel in entgegengesetzter Richtung zur Gasströmung während des Adsorptionsvorganges geiäart. Man war bisher bestrebt, vor Beginn jedes einzelnen Adsorptionsvorganges das Ad sorptionsmittel möglichst weitgehend zu desor-

Erfindungsgemäß wird von dieser Regel erheblich

abgebrochen, welcher in der Nähe des Zeitpunktes liegt, bei dem die Beladung des Spülgases mit dem desorbierten Bestandteil absinkt. Der infolgedessen nur unvollkommen desorbierte Adsorber wird an- 20 schließend wieder auf Adsorption geschlief und möglichst so lange beiaden, als er vol. malime-tähig ist, um anschließend nach Umsel ung der Adsorber, erfindungsgemäa wie ier d Lavollkommenen Desorption unterzege u we len.

Es ist ersichtlich, tab ben ...du: (em...3en Verfahren der regenerarte A. a er i ter sonst gleichen Bedingungen sehneller wiede betriebsbeneit ist als bei vollkommener Desorptio... Der be-besteht darin, daß für die unvolksommere Desorpabgewichen und die Desorption zu einem Zeitpunkt ! tion nur wenig Spülgas bzw. Energie gebraucht



( Thanked on the frace of the hill han per form of fully 8, 1949)

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AUSGEGEBEN AM 26. MXRZ 1953

PATENTS CHRIFT

Mr. 871 886

KLASSE 12e GRUPPE 302 (class) G.105 IV b/12e (July)

Dipl.-Chem. Dr.-Jug. Heinrich Kahle, Pullach bei München ist als Erfinder genannt worden (is nomid as inventer)

> Gesellschaft für Linde's Eismaschinen A.-G., Höllriegelskreuth bei München (adderption - Process-)

> > Adsorptionsverfahren

Der Zeitraum vom 8. Mai 1945 bis einschließen 7. Mai 1950 wird auf die Patentiauer nicht angerechnet

Lauf 1967 bis einschließen 7. Mai 1950 wird auf die Patentiauer nicht angerechnet

Patentameldung bekanntgemacht am 27. September 1953

Patenterteilung bekanntgemacht am 19. Februar 1953

Es ist bekannt, zur Entfernung oder Gewinnung ! von Mischungsbestandteilen aus Gasgemischen Adsorptionsveriahren anzuwenden und mit Adsorptionsmitteln gefüllte Behälter, die sogenannten Ad-5 sorber, paarweise anzuordnen, welche zum Zweck der A sorption und Desorption periodisch umgeschaltet werden. Bei der Desorption durch Spülung mittels eines Gases oder durch Evakuierung wird das Gas in der Regel in entgegengesetzter Richtung

o zur Gasströmung während des Adsorptionsvorganges geführt. Man war bisher bestrebt, vor Beginn jedes einzelnen Adsorptionsvorganges das Adsorptionsmittel möglichst weitgehend zu desorbieren.

Erhadungsgemäß wird von dieser Regel erheblich abgewichen und die Desorption zu einem Zeitpunkt

abgebrochen, welcher in der Nähe des Zeitpunktes liegt, bei dem die Beladung des Spülgases mit dem desorbierten Bestandteil absinkt. Der infolgedessen nur unvollkommen desorbierte Adsorber wird anschließend wieder auf Adsorption geschlief und möglichst so lange beladen, als er vol. ....a.mefähig ist, um anschließend nach Umsell lang der Adsorber, erfindungsgemät wie ler d unvollkommenen Desorption unterzege u we leat.

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wird, willrend bei der weitergehenden Desorption nach den bekannten Verfahren das erforderliche Spülgasvolumen nach einer Exponentialfunktion, d. h. unverhältnismäßig stark austeigt oder eine starke Temperaturerhöhung notwendig ist.

Obwohl erindungsgemält nur unvollkommen desorblert wird, kann während des Adsorptionsvorganger the gleiche Reinheit (Adsorptionswirkung) des Gases wie im Anschluß an eine vollkommene

Desorption erreicht werden.

Versuche haben erwiesen, daß für die vollkommene Reinigung des Gases bei häufig wiederholter Adsorption kereits eine Schichtiänge von 1 m genügt. Bei gröderer Schichtlänge kann die Um-

schaltung seltener vorgenommen werden.

Die Lekannten, für Adsorption und Desorption angewenderen Hilf-smaßnahmen, wie Kühlung während der Adsorption und Anwärmung oder Drucksenkung, eventuell auch unter Atmosphärendruck, während der Desorption u. dgl., können natürlich auch beim erundungsgemäßen Verfahren hinzagezogen werden. Die Ersparnis an Spülgas bzw. Energie besteht auch in diesen Fällen. Es ergeben sich somit im wesentlichen folgende Möglichkeiten zur Durchführung des erfindungsgemäßen Veriahrens:

a) Wenn bei der Ad- und Desorption gleiche, und zwar etwa Raumtemperaturen angewendet werden, so genügt es, wenn das Spülgasvolumen das 1-, 3-30 bis 21ache des Rohgasvolumens beträgt. Dementsprechend kann z. B. bei Gaszerlegungsverfahren ein in den Strom des unter Druck stehenden Roligases geschalteter Adsorber durch ein gasförmiges entspannies oder unter Unterdruck abgesaugtes Zerlegungsprodukt gleicher Temperatur oder darch einen Teil desselben desorbiert werden. Bei genügend großen Druckunterschieden kann dann sogar ein Teil des betrefienden Zerlegungsproduktes, welches nicht zum Spülen des Adsorbers gebraucht wird, rein gewonnen werden. Andererseits ist hierbei die Anreicherung des desorbierten Bestandteiles im Spülgas besonders hoch, was für die eventuelle Gewinnung des Bestandteiles günstig ist. Diese Vorteile gelten zum Teil auch für die nachstehenden Möglichkeiten.

b) Wenn für die Desorption eine höhere als die Adsorptions- oder Raumtemperatur angewendet wird, so kann das Spülgasvolumen weiter erheblich vermindert werden. Eine Temperaturerhöhung von z. B. 26 auf 100" ermöglicht eine Herabsetzung des Spülgasvolumens auf 1/30 bis 1/20 des Rohgas-

e) Sind die Gasvolumen bei der Ad- und Desorption annähernd gleich, so genügt für die Desorption eine Temperaturerhöhung um etwa 5°, vorausgesetzt, dan die Adsorption bei Temperaturen erfolgt, die nicht allzu stark von der Raumtemperatur abyeichen.

d) Erfolgen Ad- und Desorption bei tiefen Temperatures, z. B. bei - 100' oder darunter, so muß wegen der schlechteren Desorptionsmöglichkeit bei diesen Temperaturen das Spülgasvolumen das 2,5 bis 101ache des Rohgasvolumens betragen. Auch

in diesem Fall ergibt sich eine erhebliche dinsparung an Spüigas im Vergleich zu den Spüigasmengen, die bei vollkommener Desorption nötig sind.

Nach dem eründungsgemäßen Verlahren ist es möglich, die Restbeladung des gereinigten Gases für die Dauer auf geringer Vöhe zu erhalten. Legt man Wert auf besonders bese Reinheit, so genügt es, beim erfindungsgemäßer. Verfahren nach einer größeren Anzahl von Umschaltungen eine einmalige, stärkere Desorption beider Adsorber unter Anwendung einer größeren Spülgasmenge oder 75 höberer Temperaturen durchzuführen. Wie oft, diese zusätzliche Desorption erforderlich ist, muß sich nach den jeweiligen Betriebsverhältnissen richten. Es durite aber kaum Fälle geben, in denen eine solche zusätzliche Desorption öfter als nach einigen hundert Umschaltungen erforderlich wird. d. h. also, daß solche zusätzlichen Desorptionen in den erwähnten Ausnahmefällen nur in Abständen von mehreren Tagen oder Wochen erforderlich sind.

An Hand der graphischen Darstellungen (Abb. i bis 5) wird der Verlauf des Ad- und Desorptionsvorganges bei dem erfindungsgemäßen Verfahren im Vergleich zu den bekannten Verfahren erlättert.

In sämtlichen Abbildungen stellen die Ordinaten die Länge des Adsorbers in Strömungsrichtung und die Abszissen den Beladungsgrad dar, wobei Beladungsgrad 1,0 die maximale Beladungsmöglichkeit bei einer bestimmten Konzentration des zu adsorbierenden Bestandteiles im Gase, also die dem Partialdruck der zu absorbierenden Gaskomponente und der Temperatur entsprechende Sättigung des Adsorbens, bedeutet.

In Abb. 1 stellt die Kurve O.4 die Beladungsfront am Schluß einer Adsorptionsperiode dar, wenn das unreine Gas in Pfeilrichtung strömt. Am 100 unteren Ende des Adsorbens herrscht also die Beladung Null oder unter Umständen auch die zulässige Beladung (wenn keine vollkommene Entfernung des betreffenden Gasbestandteiles beabsichtigt ist), so daß bis zum letzten Zeitpunkt vor der 105 Umschaltung Gas gewünschter Reinheit aus dem Adsorber austritt. Oberhalb des Punktes A ist der

Adsorber voli beladen. Abb. 2 stellt den Zustand am Schluß einer Desorptionsperiode bei dem bekannten Verfahren 110 dar. Der Adsorber ist fast vollständig entladen; am oberen Ende des Adsorbers bei B herrscht meistens noch ein geringer Beladungsgrad E, während der Adsorber bis zur Höhe D vollkommen desorbiert ist, soweit dies durch das verwendete Spülgas mög- 115 lich ist. Die Fläche BDE stellt die Restlieladung dar, die in der Regel gering ist.

Während bei dem erfindungsgemäßen Verfahren am Schluß einer Adsorptionsperiode genau wie beim bekannten Verfahren der durch Abb. i dag- 120 gestellte Beladungszustand besteht, wird erindungsgemäß die Descrption nur so lange durelgelaurt. his die Beladungsfront, die in der Abb. 1 durch die Kurve O.A dargestellt wird, bis zur Kurve F.C. (Abb. 3) zurückgeschoben ist, wobei das Spälgas 125 am oberen Ende aus dem Adsorber noch mit einer

wesentlichen Beladung austritt. Sein Gehalt an dem desorbierten Bestandteil würde aber auschließend, bei Aufwendung entsprechend großer Spulgasmengen oder höherer Temperaturen merklich ab-5 sinken.

Es kömmt bei der Durchführung der Erindung nicht darauf an, dall dieser Zeitpunkt zur Umschaltung haarscharf erfallt wir I. Es wird sich vielmehr empfehlen, einige Zeit das Spälgas zu analysieren und zu warten, bis sein Gehalt an dem desorbierten Bestandteil absinkt und danach die zweckmäßige Desorptionsdauer bzw. die Umschaltzeit der beiden Adsorber festzulegen, eventuell unter geringer Abkürzung oder Verlängerung des für die unvollkommene Desorption ermittelten Zeitraumes, je nachdem, ob auf vollkommene Adsorption oder geringe Umschaltverluste Wert gelegt wird.

Die Fläche OACED, Abb. 4, stellt die Beladung dar, welche bei dem bekannten Verfahren nach jedem Adsorptionsvorgang desorbiert werden muß, während die Fläche OACF, Abb. 5, die Beladung darstellt, welche beim Verfahren nach der Eründung jeweils zu desorbieren ist, wobei die Ersparnis durch die Fläche FCED dargestellt wird. Da nun aber, wie bereits eingangs erläutert, für geringe Beladungsgrade sehr viel mehr Spülgas bzw. Energie zum Abbau gleicher Beladungsmengen aufgewendet werden muß, als bei voller Beladung, so ergibt sich die eingangs erläuterte wesentliche Spülgas bzw. Energiezersparnis beim erfindungsgemäßen Verfahren.

Obwohl das Spülgas aus dem Behälter vollbeladen austritt, ist doch, wie der Linienzug F C (Abb. 3 und 5) zeigt, ein großer Teil des betreffenden Adsorbers, soweit dies durch das verwendete Spülgas möglich ist, desorbiert worden, was dadurch erreicht wird, daß dasselbe Spülgas, welches bis zum Schluß aus dem Adsorber praktisch vollbeladen austritt, in denselben am anderen Ende unbeladen eingetreten ist und daher diesen Teil des Adsorbers zu desorbieren vermag.

Abweichungen von den dargestellten Kurven, z. B. innerhalb der Grenzkurven GH und JK

(Abb. 5) können aus betrieblichen Gründen unter Umständen notwendig sein und sind im Rahmen 45 des erändungsgemäßen Verfahrens zulässig.

#### PATENTANSPRÜCHE:

1. Verfahren zur Entfernung oder Gewinnung adsorbierbarer Bestandteile aus strömenden Gasgemischen durch Adsorption und anschließende Desorption, dadurch gekennzeichnet, daß die Desorption zu einem Zeitpunkt abgebrochen wird, welcher in der Nähe des Zeitpunktes liegt, bei dem die Beladting des Spülgases mit dem desorbierten Bestandteil absinkt

2. Verfahren nach Anspruch i bei Anwendung annähernd gleicher Temperaturen zur Ad- und Desorption, dadurch gekennzeichnet, daß das Spülgasvolumen das 1-, 3- bis 2fache des Rohgasvolumens beträgt.

3. Verfahren nach Anspruch i bei Anwendung einer Spülgastemperatur, die annähernd um 80° höher ist als die Adsorptions- oder Raumtemperatur, dadurch gekennzeichnet, daß das Spülgasvolumen 1/30 bis 1/20 des Rohgasvolumens beträgt.

4. Verfahren nach Anspruch t bei Anwendung annähernd gleicher Gasvolumen für Ad- und Desorption, dadurch gekennzeichnet, daß die Desorption bei nur etwa 5° höherer Temperatur erfolgt als die Adsorption.

5. Verfahren nach Anspruch i bei Anwendung tiefer Temperaturen bei der Ad- und Desorption, z. B. unter — 100°, dadurch gekennzeichnet, daß das Spülgasvolumen das 2-, 5- bis 10fache des Rohgasvolumens beträgt.

6. Verfahren nach Anspruch i bis 5, dadurch gekennzeichnet, daß nach einer größeren Anzahl von Umschaltungen beide Adsorber einer einmaligen, stärkeren Desorption durch Anwendung größerer Spülgasmengen und/oder höherer 85 Temperaturen unterzogen werden.

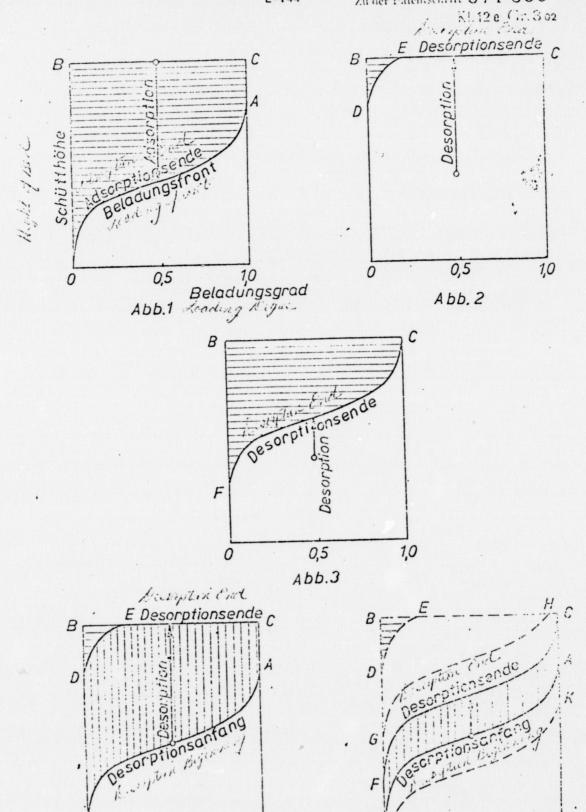
Hierzu 1 Blatt Zeichnungen



0,5

Abb.5

1,0



0,5

Abb.4

1,0

It is known that one can use adsorption processes for the removal or obtaining of mixture components of gas mixtures by using . adsorbers which are arranged in pairs and which are periodically switched for the purpose of adsorption and desorption. During desorption through purging with a gas or through evacuating, the gas flow is, as a rule, in the opposite direction of the gas flow during the adsorption process. Up to now, the aim was to desorb the adsorption means (desiccant) to the greatest extent possible prior to the beginning of each adsorption process.

This invention deviates from this rule considerably and desorption is stopped at a point when the loading of the purge gas with the component that is to be desorbed is diminishing. The adsorber, which consequently is only incompletely desorbed, is subsequently switched to adsorption again and is being loaded as long as it is capable to be loaded, and is subsequently, after switching of the adsorber, again desorbed incompletely in accordance with this invention.

It is evident, that in accordance with this invention, everybeing equal, the regenerated adsorber gets back into operation quicker than with complete desorption. The special advantage of the process per this invention is that for the incomplete desorption only little purge gas, respectively energy, is required, while for extensive desorption in accordance with the known processes the required purge gas volume increases exponentially, or a high temperature increase is necessary.

Although the desorbing in accordance with this invention is only incomplete, the same purity of the gas during adsorption can be obtained as after a complete desorption.

Experiments have shown that for the complete purifying of the gas by frequent, repeated adsorption, even a desiccant column of one meter is sufficient. By greater column lengths the switching can take place less frequently.

The usual assists for adsorption and desorption, like cooling during adsorptionand heating or pressure reduction, eventually also less than atmospheric pressure, during desorption etc., can of course be utilized in the procedure per this invention. The

savings on purge gas, respectively energy, exist also in these cases. Therefore, the following possibilities essentially exist in executing the process per the invention:

- If during ad- and desorption the same and approximate ambient temperatures are being utilized, then it is sufficient if the purge gas volume is one, two, or three times the raw gas volume. Accordingly, in the gas fractionation process an adsorber which has been in the stream of raw gas under pressure can be desorbed, by means of a fractionation product or a part of it which is depressurized or was removed by vacuum, at the same temperature. With sufficiently large pressure differential, a part of the fractionation product in question, which is not needed for the purging of the adsorber, can then even be obtained pure. On the other hand, the enrichment with the desorbed component is particularly high in the purge see which is an education. particularly high in the purge gas, which is an advantage for the eventual obtaining of the component. These advantages are valid in part also for the following possibilities:
  - If a higher temperature is used for desorption than the adsorption or ambient temperature, then the purge gas volume can be reduced considerably further. For example, a temperature increase from 20 to 100 degrees C. allows b) a reduction of the purge gas volume to 1/30 to 1/20 of the raw gas volume.
  - If the gas volumes during adsorption and desorption are approximately the same, then it is sufficient to increase the desorption temperature by approximately 5 degrees, assuming therby that the adsorption takes place at a c) temperature which does not vary greatly from the ambient temperature.
  - If the adsorption and desorption take place at low temperatures, for example -100 degrees or lower, then the purge gas volume has to be 2½ to 10 times the raw gas volume on account of the bad desorption conditions at d) these temperatures. In this case, too, there is a considerable saving on purge gas when compared to the quantity of purge gas required with complete desorption.

In accordance with this invention, it is possible to keep the residual loading of the purified gas very small permanently. If one is concerned with especially high purity, then it is sufficient in this invention to undertake a stronger desorption of both adsorbers by means of a larger purge gas volume or a higher temperature one time after a larger number of cycles. How often this additional desorption is required depends on the respective operating conditions. However, there hardly should be a case in which such additional desorption is required more frequently than after a few hundred cycles, this means, therefore, that such additional desorption in the exceptional cases is only required at intervals of several days or weeks.

On hand of drawings 1-5 the process of ad- and desorption of this invention is compared with the known process.

In all drawings the ordinate represents the height of the adsorber in the direction of the flow and absissa represents the degree of loading, whereby one is the maximum loading capacity at a certain concentration of the gas component which is to be adsorbed, in other words, representing the corresponding saturation of the desiccant corresponding to the partial pressure of the gas component which is to be adsorbed, and the temperature.

In drawing 1 the curve OA represents the loading front at the end of an adsorption period, with the unpure gas flowing in the direction of the arrow. Therefore, at the lower end of the desiccant there exists no loading at all or under the circumstances also a parial loading (when it is the intention not to achieve a complete removal of the respective gas component.) So that, therefore, up to the very last moment prior to the cycling, gas of the desired purity can be obtained from the adsorber. Above point A the adsorber is fully loaded.

Drawing 2 shows the situation at the end of the desorption pweriod of the commonly known process. The adsober is almost entirely unloaded. At the upper end of the adsorber at B, there most times is still a small loading E, while the adsorber is completely desorbed up to the height D to the degree that this is possible with the purge gas utilized. The area BDE represents the residual loading which as a rule is small.

While the process at the end of the adsorption period under the commonly known procedure as shown in Drawing #1 is the same as the process described in this invention, the desorption in accordance with this invention is only performed until the loading front, which is shown in Drawing #1 by the curve OA, is pushed back to curve FC in Drawing #3, whereby the purge gas at the upper end of the adsorber leaves with still a substantial loading. The content of desorbed component would, however, subsequently reduce itself noticeably with utilization of correspondingly larger purge gas volumes or higher temperature.

In the utilization of this invention, it is not critical that the point of switch-over be precisely determined. It is, on the contrary, recommended to analyze for some time the purge gas and wait until its content of desorbed component diminishes and then to establish appropriate desorption time, respectively cycling time of the two adsorbers, eventually with some shortening or lengthening of the time interval for incomplete desorption, depending whether one looks for complete adsorption or small cycling losses.

The area OACED, Drawing 4, represents the loading which per the commonly known process has to be desorbed after each adsorption cycle, while the are OACF, Drawing 5, represents the loading which has to be desorbed per the process of this invention, whereby the saving is represented by the area FCED. As previously explained, for a low degree of loading, much more purge gas, respectively energy, has to be used to remove an equal quantity of lad than is necessary at full loading, therefore, the savings of substantial purge gas, respectively energy, in the process per this invention, is clear as explained above.

Although the purge gas is leaving the container fully loaded as shown in the line FC of drawings 3 and 5, a large part of the respective adsorber has been desorbed, to the extent that this is possible, through the use of the purge gas used. This was acheived because this purge gas, which leaves the adsorber practically fully loaded, entered the adsorber at the other end unloaded, and therefore was able to desorb this part of the adsorber.

Variations from the pictured curves, for example within the limit-curves of GH and JK, Drawing 5, might be necessary for operational reasons and circumstances and are proper within the framework of this invention.

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- 1. Process for removal or obtaining of adsorbable components of flowing gas mixtures through adsorption and subsequent desorption characterized by the desorption being broken off at a point which is near the point when the loading of the purge gas with the desorbable component diminishes.
- 2. Process per Claim 1 using approximately the same temperature for ad- and desorption, characterized by the purge gas volume being on, two, three times the raw gas volume.
  - 3. Process in accordance with Claim 1 using a purge gas temperature which is about 80 degrees higher than the adsorption for ambient temperature, characterized by the purge gas volume being 1/30-1/20 of the raw gas volume.
  - 4. Process per Glaim 1 using about the same gas volume for ad- and desorption, characterized by the desorption taking place at only about 5 degrees higher temperature than the adsorption.
  - 5. Process per Claim 1 using lower temperatures at adand desorption, for example, below -100 degrees, characterized by the purge gas volume being two, five, to ten times the raw gas volume.
- 6. Process per Claims 1 through 5 characterized by a stronger desorption by larger purge gas volumes and/or higher temperatures after a greater number of cycles.

## DEFENDANTS' EXHIBIT M(5)

21. Kahle German Patent No. 970,223 and Translation

Erteilt auf Grund des Ersten Überleitungsgesetzes vom 8. Juli 1949

purble of Sumary BUNDESREPUBLIK DEUTSCHLAND

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Dipl.-Chem. Dr.-Jug. Heinrich Kahle, Pullach bei München ist als Erfinder genannt worden

( is marked con entinter)

Gesellschaft für Linde's Eismaschinen A.-G., Höllriegelskreuth bei München

Verfahren zur Abtrennung adsorbierbarer Bestandteile

Patentiert im Gebiet der Bundesrepublik Deutschland vom 26. November 1948 an Patentanmeldung bekanntgemacht am 23. Mai 1951 Patenterteilung bekanntgemacht am 14. August 1958 (14, 1958)

Es ist bekannt, adsorbierbare Bestandteile von Gasgemischen mittels periodisch umschaltbarer, durch adsorbatfreies Spülgas regenerierbarer Adsorber zu entfernen. Dabei ist es in der Adsorptionstechnik allgemein üblich, daß Adsorbens nur bis zu etwa 50 bis 75% seiner maximalen Aufnahmefähigkeit, die als Gleichgewichtsbeladung bezeichnet wird, zu beladen. Der als Durchbruchsbeladung bezeichnete Wert ist dann erreicht, wenn die Konzentration des zu adsorbierenden Bestandteiles im Endprodukt von einem kleinen konstanten oder nur

wenig sich ändernden Wert plötzlich beschleunigt anzusteigen beginnt.

Das Bestreben geht in der Technik stets dahin, Bedingungen aufzusuchen, bei denen die Aufnahmefähigkeit des Adsorbens gesteigert wird. Dämpfe der Gasbestandteile, deren flüssige Phase auch bei gewöhnlicher Temperatur existiert, wie die Dämpfe von Wasser oder organischen Lösungsmitteln, werden bereits bei gewöhnlicher Temperatur durch Adsorptionsmittel, wie Gel, so leicht adsorbiert, daß man in der Nähe ihres Taupunktes je nach Schichtlänge Durchbruchsbeladungen zwischen 55 und 80% der Sättigungsbeladung von 35 Gewichtsprozent, d. h. eine Gesamtbeladung von etwa 20 Gewichts prozent, erzielt. Benzol wird unter ähnlichen Bedingungen und in ähnlicher Größenordnung von Aktivkohle adsorbiert. Anders liegen die Verhältnisse, wenn man versucht, tiefsiedende Gase, wie z. B. die Kohlensäure der atmosphärischen Luft, durch Adsorption weit unterhalb ihrer Taupunktskonzentratien zu entfernen. Bei dem Partialdruck der in der Luft befindlichen Kohlensäure, nämlich 0,2 mm Hg, erzielt man bei gewöhnlicher Temperatur nur eine Gleichgewichtsbeladung von etwa 0.32 ccm CO<sub>2</sub>/g Kohle = ~ 0.06 % des Kohlegewichtes. Sucht man etwa die Luft durch Adsorption über Kohle zu reinigen und in der üblichen Weise letztere etwa bis zur Hälfte dieses Gleichgewichtswertes zu beladen, so kommt man trotzdem zu keiner genügenden Reinigung. Wie Versuche zeigten, ist erst bei einer wesentlich kleineren Beladung, die bei etwa 0,07 ccm/g Adsorbens = 22 % der Gleichgewichtsbeladung liegt, die Entfernung der Kohlensäure aus dem Gas bis zu einem verlangten Reinigungseffekt von etwa 99 % ausreichend. (Bei geringeren Anforderungen an den Reinigungseffekt können höhere Beladungen zugelassen werden.) Nach den normalen Gesichtspunkten in der Adsorptionstechnik erscheint es also zunächst aussichtslos, unter diesen Bedingungen an eine technisch weitgehende Entfernung tiefsiedender Gase auf diesem Wege zu denken, da untragbar hohe Adsorbensmengen aufgewendet werden müßten. Eine wesentliche Verkürzung der Umschaltzeiten (um Adsorbens zu sparen) stößt auf die Schwierigkeit, daß bei der Desorption die bisher übliche Erwärmung und Wiederabkühlung des Adsorbens auf die Adsorptionstemperatur nicht in genügend kurzer Zeit du chgeführt werden kann, zumal da gerade das Adsorbat, das in kleiner Konzentration auf dem Adsorbens sitzt, schwierig zu entfernen ist.

Überraschenderweise wurde jedoch durch Versuche gefunden, daß die Regenerierung, auch bei kleinen Beladungen, in kurzer Zeit möglich ist, wenn man bestimmte Bedingungen einhält. So war es möglich, mit einem dauernd extrem hohen Reinigungseffekt von 99 % auch kleinste Mengen tiefsiedender Gase, wie CO<sub>2</sub>, bei gewöhnlichem Druck und gewöhnlicher Temperatur aus Gasgemischen, wie Luft, praktisch vollständig zu entfernen, wenn man das Adsorbens, ausgehend von einer Restbeladung, nur bis zu etwa 20 bis 25 % šeiner Gleichgewichtsbeladung mit dem abzuscheidenden Gas, wie CO<sub>2</sub>, belädt und bereits vor Erreichung des Durchbruchs den zugeladenen Betrag bei gleicher Temperatur mit überschüssigem Spülgas wieder entfernt.

Wie die Versuche weiter zeigten, waren 10 Minuten ausreichend, um den zugeladenen Betrag ohne Temperaturerhöhung, also bei der gleichen Temperatur mit etwa dem Drei- bis Vierfachen des effektiven Rohgasvolumens an Spülgas zu entfernen. Unter Effektivvolumen ist das tatsächlich vom Gas eingenommene Volumen zu verstehen, das sich bei gleichem Gasgewicht etwa umgekehrt proportional zum

Druck ändert. Die verbliebene Restbeladung Letrug unter diesen Verhältnissen etwa 8 %, die jeweils zugeladene Menge etwa 14% des Gleichgewichtswertes. Sie wird im folgenden als Zuladung gekennzeichnet. Weitere länger dauernde Versuche zeigten, daß der gleiche Reinigungseffekt auf die Dauer aufrechterhalten werden konnte und daß für andere 70 Gase ähnlicher Eigenschaften ähnliche Verhältnisse bestehen. Für eine weitgehende Reinigung ist wichtig, daß die Zuladung auch nicht bis zum Durchbruch der abzuscheidenden Komponente erfolgt. sondern bei höchstens 90 % der Durchbruchsbela- 75 dung abgebrochen wird. Auf diese Weise bleibt eine genügende Schicht völlig unbeladenen Adsorbens erhalten, welche den äußerst hohen Reinigungseffekt vor Erreichung des Durchbruchs bedingt.

Das Wesen des vorliegenden erfindungsgemäßen 80 Verfahrens zur Abtrennung adsorbierbarer Bestandteile aus Gasgemischen mittels periodisch wechselbarer Adsorber durch adsorbatfreies Spülgas besteht also darin, daß man das Adsorbens nur bis zu einem unter 50 % seiner Gleichgewichtsbeladung sowie unter 90 % seiner Durchbruchsbeladung liegenden Wert auflädt und dann auf den zweiten, inzwischen von der Zuladung befreiten (teilentladenen) Behälter umschaltet, wobei Umschaltzeiten zwischen 5 und 30 Minuten angewendet werden. Bei 90 etwa Atmosphärendruck bewegt man sich in der Nähe der unteren Grenze für die Umschaltzeit, bei erhöhtem Druck in der Nähe der oberen Grenze von etwa 30 Minuten, da mit erhöhtem Druck auch die Aufnahmefähigkeit des Adsorbens steigt. Desglei- 95 chen wird bei erstrebtem hohem Reinigungseffekt die Umschaltzeit mehr der unteren Grenze genähert. Jmschaltzeiten werden angewendet, Diese kleir um die Meage des Adsorbens bis zu einem wirtschaftlich noch tragbaren Wert herabzusetzen. Die 100 erfindungsgemäße untere Grenze der Umschaltzeit wird man dabei jedoch nicht unterschreiten können, da das Trägergas für die Verunreinigungen, das meist rein gewonnen bzw. verarbeitet werden soll, teilweise mitadsorbiert wird und dieser Teil bei der 105 nachfolgenden Spülung verlorengeht.

Es ist zwar bereits vorgeschlagen worden, kürzere Umschaltzeiten zu verwenden, die z. B. unter einer halben Stunde liegen können, wie es z. B. die deutsche Patentschrift 624912 im Anspruch 5 vor- 110 schreibt. Dieses Verfahren arbeitet jedoch insofern anders, als die Verkürzung der Umschaltdauer nicht etwa wegen der Absicht, die Beladungshöhe des Adsorbens zu verringern, variiert wurde, sondern wegen der Notwendigkeit, die Verweilzeit der auf dem 115 Adsorbens sitzenden, neben Benzol abgeschiedenen polymerisierenden Verunreinigungen zu verkürzen, die das Adsorbens unbrauchbar machen. Das Adsorbens wird daher stärker belastet und das Gas mit größerer Geschwindigkeit hindurchgeführt. Dies 120 soll nach Anspruch 1 der Patentschrift dadurch erreicht werden, daß »die Adsorbensmenge im Verhältnis zu der aus den pro Tag zu verarbeitenden Gasen gewinnbaren Kohlenwasserstoffmenge geringer als 2:1 gchalten wird«. Im Gegensatz zum er- 125 findungsgemäßen Verfahren wird also die Belastung des Adsorbens erhöht. Die Desorption erfolgt durch gleichzeitiges indirektes Heizen und Ausdämpfen, also praktisch vollständig und nicht teilweise, wie nach dem erfindungsgemäßen Verfahren, sowie durch Anwendung von unkondensierbaren Spülgasen. Auch wird die maximale Beladung nicht auf höchstens 90 % der Durchbruchsbeladung beschränkt.

Es ist ferner ein anderes Verfahren nach Patent 704 073 mit kurzfristiger Umschaltung vor Erreichung des Adsorptionsgleichgewichtes angegeben worden, bei dem aber nur eine lediglich wasserstoffreiche (also noch Kohlenoxyd enthaltende) Fraktion aus einem Kohlendioxyd-Wasserstoff-Gemisch gewonnen wird. Es wird also hierbei kein Wert darauf gelegt, daß die Beladung des Adsorbens mit dem zu entfernenden Gasbestandteil auf höchstens 90 % der Durchbruchsbeladung beschränkt wird.

Erfindungsgemäß wird durch diese Maßnahme gewährleistet, daß, wie bereits erwähnt, eine genügende Schicht Adsorbens von Adsorbat völlig frei gehalten wird und das austretende Gas frei ist von der zu adsorbierenden Gaskomponente. Die Tatsache, daß durch das erfindungsgemäße Verfahren auch noch eine hohe Reinheit der behandelten Gase ermöglicht wird, ist um so überraschender, als auf hohe Desorptionstemperaturen verzichtet und das Adsorbens bei gleicher oder nur wenig höherer Temperatur nur teilweise entladen wird.

Der Reinigungseffekt ist ein besonders hoher, wenn bei der Teilentladung das adsorbatfreie reine Spülgas entgegengesetzt zur Rohgasrichtung durch das Adsorbens strömt. Dabei wird das Spülgas so gut ausgenutzt, daß erfindungsgemäß bereits ein Spülgasvolumen gleich dem Drei- bis Vierfachen des Rohgasvolumens ausreicht, um bei Umgebungstemperatur sowie bei der gleichen Temperatur das Adsorbat so weit zu entladen, daß ein gleichbleibender Reinigungseffekt von mehr als 99% für die Dauer gewährleistet wird, ohne daß Spülgas über die Rohgastemperatur angewärmt werden muß. Das Verfahren kann prinzipiell mit allen Adsorbensarten durchgeführt werden. Es ist aber zweckmäßig, mit Adsorbentien besonders hohen Adsorptionsvermögens zu arbeiten und erfindungsgemäß bevorzugt mit solchen, die auf Grund der selektiven Adsorption der abzuscheidenden Bestandteile diese besonders stark zu binden vermögen, während das Trägergas relativ weniger leicht adsorbiert wird. Desgleichen wurde ein großer Einfluß der Körnung des Adsorbensmaterials in dem Sinne gefunden, daß mit feinerer Körnung der Wirkungsgrad der Reinigung steigt. Dieses ist zwar qualitativ theoretisch vorauszusehen, es ist jedoch zweckmäßig, mit Rücksicht auf die Gefahr des Mitreißens bei sehr kleiner Körnung und auf den hohen Druckabfall, der infolge des bei Verwendung von feiner Körnung steigenden Wirkungsgrades entsteht, keine übermäßig kleine Körnung, sondern nach einem weiteren Erfindungsgedanken Körnungen von 1 bis 2 mm anzuwenden, da es in diesem Bereich noch möglich ist, mit erträglichen Druckabfällen zu arbeiten, besonders wenn dabei erfindungsgemäß Querschnitte der

Adsorbensschicht zwischen 0,5 und 1 qm pro 1000 cbm stündlich strömendes Gas angewendet werden. Die Adsorbensschicht soll dabei mit Rücksicht auf den erstrebten hohen Reinigungseffekt mindestens 1,5 m lang sein. Die obere Grenze dieses Wertes richtet sich nach dem zulässigen Druckabfall und dem mit Rücksicht auf die Mitadsorption 70 des Trägergases begrenzten Aufwand an Adsorbensmenge.

Steht das Gas unter Druck, wobei das Effektivvolumen des verdichteten Gases dem Druck umgekehrt proportional ist, so ist nach einem weiteren 75 Erfindungsgedanken das Volumverhältnis 1:3 bis 4 zwischen Rohgas und Spülgas gewährleistet, wenn der Druck des Rohgases mindestens drei- bis viermal höher ist als der des Spülgases. Ist also z. B. das Normalvolumen, gemessen bei 1 ata, von Roh- 80 gas und Spülgas gleich und der Spülgasdruck = 1,1 ata, so reicht ein Rohgasdruck von 3,3 bis 4,4 ata aus, um dem nach obigem vorgeschriebenen Verhältnis 1:3 bis 4 als unterer Grenze zu genügen. Ist der Reinheitsgrad nicht ausreichend, so kann 85 durch Erhöhung dieses Verhältnisses oder, wenn dies nicht möglich ist, durch Verkürzung der Umschaltzeit in den obigen Grenzen eine Verbesserung erreicht werden, sofern der Verlust an Trägergas noch erträglich ist.

Reicht die zur Verfügung stehende Spülgasmenge nicht aus, so genügt eine Anwärmung um wenige Grade, um unter den gegebenen Bedingungen mit noch kleineren Spülgasmengen auszukommen. Für je eine Halbierung der Verhältniszahl 3 95 ist eine Erhöhung des mittleren Temperaturniveaus der Teilentladung von 3°C (untere Grenze) gegen-über dem Zuladungsvorgang ausreichend. Durch diese rationelle Ausnutzung des Spülgases und durch den Wegfall von großen Energien zu seiner 100 Vorerhitzung wird der Umstand aufgewogen, daß die Adsorbensmenge infolge ihrer geringen Beladung immerhin noch relativ groß sein muß. Andererseits ist der Umstand günstig, daß infolge der dabei anzuwendenden größeren Querschnitte der 105 Adsorber der Druckverlust des strömenden Gases kleiner und der Energieaufwand zur Überwindung des Strömungswiderstandes geringer ist. Das allgemeine Temperaturniveau der Beladung und Entladung kann je nach Umgebungstemperatur höher 110 oder tiefer sein. Durch Verkürzung oder Verlängerung der Umschaltzeiten wird man sich den veränderten Bedingungen anpassen können, ohne wesentliche Änderungen an dem Verhältnis von Spülgas zu Rohgasmenge vornehmen zu müssen. 115 Man kann auch, um mit wesentlich kleineren Adsorbensmengen auskommen zu können, erfindungsgemäß bei tieferem Temperaturniveau arbeiten als es die Umgebung aufweist, insbesondere wenn ohnehin das Rohgas aus Gründen der weiteren Zer- 120 legung abgekühlt werden muß.

Ist die Konzentration des abzuscheidenden Bestandteils hoch, so kann man in an sich bekannter Weise zur Abführung der Adsorptionswärme die beiden Adsorber nach Art von Wärmeaustauschern 125 ineinander bauen. Die Adsorptionswärme kommt

dabei dem Entladevorgang, die Desorptionskälte dem Beladevorgang zugute.

Ein Wärmeaustausch zwisenen beiden Vorgängen ist auch durch die an sich bekannte Nachschaltung von Speichermassen möglich, an welche die austretenden Rohgase ihre Wärme abgeben. Diese wird ihrerseits nach Umschaltung auf das Spülgas übertragen. Das gleiche Mittel kann angewendet werden, wenn das Spülgas von vornherein kälter ist als das Rohgas.

Die bei der Adsorption größerer Dampf- oder Gasmengen frei werdende Adsorptionswärme, die dem zu beladenden Adsorbens eine höhere Temperatur erteilt, kann erfindungsgemäß so ausgenutzt 15 werden, daß bereits dann umgeschaltet wird, wenn eine bestimmte Temperaturerhöhung an einer Meßstelle, z. B. in der Mitte des gerade in der Beladung befindlichen Adsorbens erreicht wird. Auf diese Weise bleibt auch die Temperaturerhöhung des Adsorbens zur Förderung der nachfolgenden Teilentladung erhalten. Es ist besonders zweckmäßig, die Temperaturerhöhung dazu auszunutzen, daß man in an sich bekannter Weise diesen Adsorber automatisch nach Auslösung einer dementsprechenden Verrichtung umschaltet. Dies kann z.B. dadurch geschehen, daß ein Kontaktthermometer bekannter Art in das Adsorbens eingebaut wird und relaisartig einen Stromkreis schließt, in dem die Umschaltvorrichtung liegt.

Das Verfahren sei an einem Beispiel näher erläutert: Luft mit 0,03% Kohlensäure wird bei 1,4 ata und gewöhnlicher Temperatur über einen von zwei parallel geschalteten Adsorbern, die mit einer Aktivkohleschicht von 1,5 m Länge gefüllt sind, mit einer Raumgeschwindigkeit von 600 cbm pro chin Adsorbens und Stunde geführt. Nach 10 Minuten Beladungszeit werden die Adsorber in bekannter Weise gewechselt und anschließend daran der beladene Adsorber mit kohlensäurefreiem Stickstoff von 1,15 ata bei gleicher Temperatur und mit einer Raumgeschwindigkeit von 2400 chm pro chm Adsorbens und Stunde gespült, während der während der Beladung des ersten Adsorbers inzwischen gespülte, teilweise entladene zweite Adsorber 45 beladen wird. Der Reinigungseffekt beträgt nach 100 Stunden Wechselbetrieb 99,5% entsprechend 0,00015 % Kohlensäure im Endgas.

Die erreichten Vorteile liegen, wie das Beispiel zeigt, in der hohen Reinigungswirkung des Adsorbens, das im vorliegenden Fall nur mit 20 % seines Gleichgewichtswertes, nämlich mit 0,07 cm3 CO2/g Kohle beladen ist, ohne daß jedoch infolge der kurzen Umschaltzeit die Adsorber unwirtschaftlich große Ausmaße erhalten. Bei höheren Gehalten an Adsorbierbarem im Rohgas liegt ein besonderer Vorteil darin, daß infolge der kurzen Umschaltzeit praktisch die gesamte Wärme des Adsorptionsvorganges im Adsorber verbleibt und somit für die anschließende Desorption nutzbar verwendet wird. Es ist somit möglich, die Entfernung von dampfförmigen Verunreinigungen aus Gasen, die man sonst gern bei höheren Drucken durchführt (wegen des geringeren relativen Dampsgehaltes) ohne Nachteil

für die Reinigungswirkung und mit geringerem Energieaufwand auch bei niedrigerem Druck durchzuführen.

#### PATENTANSPROCHE:

1. Verfahren zur Abtrennung adsorbierbarer Bestandteile aus Gasgemischen mittels periodisch wechselbarer, durch adsorbatfreies Spülgas teilweise regenerierter Adsorbentien, dadurch gekennzeichnet, daß man das Adsorbens nur bis zu einem unter 50 % seiner Gleichgewichtsbeladung und unter 90 % seiner Durchbruchsbeladung liegenden Wert auflädt, dann auf den zweiten inzwischen teilweise regenerierten Behälter umschaltet, während der erste mit überschüssigem Spülgas in entgegengesetzter Richtung teilentladen wird, wobei Umschaltzeiten zwischen 5 und 30 Minuten angewendet werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man die Teilbeladung bei Umgebungstemperatur sowie bei der gleichen Temperatur durchführt wie die Teilentladung und dabei ein Spülgasvolumen gleich dem drei- bis vierfachen effektiven Rohgasvolumen durch das Adsorbens schickt.

3. Verfahren nach Anspruch 1 und 2, dadurch gekennzeichnet, daß man Adsorbentien hoher selektiver Aufnahmefähigkeit für den abzuscheidenden Bestandteil anwendet.

4. Verfahren nach Anspruch I bis 3, dadurch gekennzeichnet, daß man Adsorbenskörnungen zwischen I und 2 mm verwendet.

5. Verfahren nach Anspruch i bis 4, dadurch gekennzeichnet, daß man Querschnitte der Adsorbensschicht von 0,5 bis i qm pro 1000 cbm stündlich strömendes Gas bei Schichtlängen von mindestens 1,5 m verwendet.

6. Verfahren nach Anspruch i bis 5, dadurch gekennzeichnet, daß man bei gleichem Normalvolumen von Rohgas und Spülgas den Druck des Rohgases bei der Beladung drei- bis viermas höher einstellt als den Druck des Spülgases.

7. Verfahren nach Anspruch 1 bis 6, dadurch 100 gekennzeichnet, daß man bei einem Unterschreiten des Volumverhältnisses Rohgas: Spülgas von 1:3 bis 4 für je eine Halbierung des Verhältnisses eine um 3 Grad höhere Temperatur (untere Grenze) des Spülgases verwendet.

8. Verfahren nach Anspruch 1 bis 7. dadurch gekennzeichnet, daß man das Temperaturniveau der Adsorption und Desorption gegenüber der Umgebungstemperatur senkt.

9. Verfahren nach Anspruch 1 bis 5. dadurch 120 gekennzeichnet, daß man in an sich bekannter Weise im Interesse eines Wärmeaustausches zwischen Beladungs- und Entladungsvorgang (bei höheren Konzentrationen der abzuscheidenden Bestandteile) beide Adsorber nach Art von 125 Wärmeaustauschern ineinander baut und auf

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diese Weise in thermischen Kontakt miteinander

10. Verfahren nach Anspruch 1 bis 9, dadurch gekennzeichnet, daß man die Adsorber automatisch umschaltet, sobald infolge größerer adsor-

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ten Meßstelle im beladenen Adsorbens erreicht ist.

In Betracht gezogene Druckschriften: Deutsche Patentschriften Nr. 624912, 704073; bierter Gas- und Dampfmengen eine vorbe-stimmte Temperaturerhöhung an einer bestimm- Bratzler, »Adsorption von Gasen und Dämpfen«, 1944, S. 107, 108, 121.

### GERMAN PATENT NO. 970223

It is known that adsorbable components of gaseous mixtures can be separated by means of adsorbate-free purge gas through cyclically switchable regenerable adsorbers. It is common practice in the adsorption technique to load the adsorbent only to about 50 to 75 percent of its maximum capacity which is called "equilibrium load." The value which is called "breakthrough load" is then reached when the concentration of the to be adsorbed component increases suddenly in the end product from a small constant or only minimally changing value.

In the technique, efforts are being made constantly to find conditions which increase the capacity of the adsorbent. The vapors of gas components, whose liquid phase also exists at normal temperatures like the vapors or water of organic solvents, are adsorbed so readily at normal temperatures by adsorbents like silica gel, that in profimity of their dewpoint and depending on length of layer, breakthrough loads between 55 and 80 percent of saturation load of 35 weight percent, this means a total load of about 20 weight percent is obtained. The conditions are different when one tries to adsorb gases of low boiling point through adsorption far below their dewpoint concentration like the CO<sub>2</sub> of the atmospheric air. With the partial pressure of the CO<sub>2</sub> contained in the air, i. e., 0.2 mm of mercury, one obtains at normal temperatures only an equilibrium loading of approximately 0.32 cmm of CO<sub>2</sub> per gram of charcoal. This is approximately 0.06 percent of the charcoal weight. When one tries to purify the air

through adsorption over charcoal and as is customary, tries to load the charcoal up to half of its equilibrium value, one nevertheless does not obtain adequate purification. As tests have shown only by a substantially smaller loading, approximately 0.07 ccm per gram of adsorbent which is approximately 22 percent of the equilibrium loading, does one obtain adequate removal of the CO2 from the gas to a desired purity of about 99 percent. (When lesser requirements of purity exist, higher loading is permissible.) Based on normal considerations in the adsorption technique, it appears hopeless, under these conditions, to think of technically extensive removal of low boiling point gases in this manner because, impractical, large quantities of adsorbent would have to be used. A substantial shortening of the cycle time to save on adsorbent, encounters difficulty in that, during desorption, the up-to-now common heating and cooling of the adsorbent to the adsorbing temperature cannot be accomplished in short enough time, especially as the adsorbate which sits in a light concentration on the adsorbent is difficult to remove.

Surprisingly, however, experiments have shown, that the regeneration, even in the case of small loadings, is possible in a short time interval when certain conditions are observed so it was possible with a constant, extremely high purifying effect of 99 percent to practically remove entirely also smaller quantities of low boiling gases, like CO<sub>2</sub>, at normal pressures and normal temperatures from gaseous mixtures, like air, when the adsorbent, starting with a residual load, was only loaded up to about 20 to 25 percent of its equilibrium load with the gas to be adsorbed like CO<sub>2</sub>, and already prior to the breakthrough being reached the added load was removed at the same temperature with

unneeded purge gas.

As experiments showed, further, ten minutes were sufficient to remove the added load without raising the temperature, in other words, at the same temperature, by means of a purge gas volume which was three to four times the effective raw gas volume. Effective volume should be understood to mean the actual volume occupied by the gas, which is inversely proportional to the pressure of the gas of the same weight. Under these conditions, the residual load amounted to 8 percent and the added load each time to approximately 14 percent of the equilibrium value. In the following, we will use the term of "add-load" for identification. Further experiments of longer duration showed that the same degree of purity could be maintained permanently/ior other gases of similar characteristics, similar conditions exist. For effective purifying it is important that the add-load is not increased to the breakthrough point of the component which is to be separated, but is stopped at the latest when 90 percent of the breakthrough load has been reached. In this manner, a sufficient layer of un-loaded adsorbent remains which is a condition for the high purity effect one obtains prior to reaching the breakthrough.

The essential of the foregoing avention to separate adsorbable components from gaseous mixtures by means of periodically cycling adsorbers through adsorbate-free purge gas is that the adsorbent is being loaded at less than 50 percent of its equilibrium load and less than 90 percent of its breakthrough load, and that one then switches over to a second container which has in the meantime been freed of its add-load (partially un-loaded), whereby a switching cycle of between

operate in the area of the lower limit of the cycle time and at higher pressure in the area of the upper limit of approximately thirty minutes because with increased pressure the adsorbing capacity of the adsorbent increases. Likewise, when one is aiming at high purity, the cycle time is to be near the lower limit. These short cycle times are being utilized in order to keep the quantities of the adsorbent economically practical. The lower limit of the cycle time given in this invention will hardly be possible to undercut, because the carrier of gas of the impurities which mostly is to obtained pure, respectively is to be utilized will be in part, also adsorbed and this part will be lost during the subsequent purging.

Admittedly, it has already been suggested to use shorter cycle times which would be less than half an hour and as for example given in patent o. 624912, i.e. Claim No. 5. This process, however, works differently in that the shortening of the cycle time did not intend to reduce the loading of the adsorbent, but was needed to reduce the duration of time during which the, in addition to the Benzol, separated polymerized impurities, which make the adsorbent unusable, were sitting on the adsorbent. The adsorbent is therefore being I aded heavier and the gas is passed through at higher speed. In accordance with Page I of that patent, this supposedly is being achieved though "the quantity of adsorbent is kept in a ratio of less than 2:1 to the CO<sub>2</sub> quantity obtainable per day. Contrary to the invention, here, the loading of the adsorbent is increased. The desorption is accomplished through concurrent heating and vaporizing; therefore,

practically complete and not partial, like in this invention as well as through the use of uncondensable purge gas. Also, the maximum loading is not limited to 90 percent of the breakthrough load.

There is furthermore another process per patent 704073 disclosed with short cycle prior to obtaining of adsorption equilibrium where, however, only a hydrogen rich fraction (therefore still containing CO<sub>2</sub>) is being obtained out of the CO<sub>2</sub> hydrogen mixture. No attention was given to limiting the loading of the adsorbent to a maximum of 90 percent of the breakthrough load.

Per invention as mentioned, already, through this requirement (by limiting the adsorption to a maximum of 90 percent of the breakthrough loading it assured that a sufficient layer of adsorbent remains entirely free of the adsorbate and the effluent gas is free of the gas component which is to be adsorbed. The fact that through this invention it is possible to obtain high purity of the process gas is still more surprising in view of the fact that high desorption temperatures are not being used and the adsorbent is only partially unloaded at the same or only slightly higher temperature.

The purifying effect is especially high when, during the partial unloading, the adsorbate-free pure purge gas flows in opposite direction to the raw gas flow through the adsorbent. In this manner, the purge gas is so thoroughly used that per this invention, even a purge gas volume of three to four times that of raw gas volume is sufficient to unload the adsorbent at ambient temperature as well as at the same temperature, so that a constant purifying effect of better than 99 percent is guaranteed permanently without that the purge gas has to be heated above the

temperature of raw gas. The process can in principle, be used in all types of adsorbents. However, it is advantageous to work with adsorbent materials that have a specially high adsorption capacity and in accordance with this invention, preferably with those that, through selective adsorption of the component which is to be separated, can bind this component strongly and will adsorb relatively dittle of the carrier gas. In this sense, it was found that the particle size of , the adsorbent material has considerable influence in that, by smaller size, the effectiveness of the purifying increases. This is to be expected, but it is for practical reasons desirable to avoid excessively small size, to avoid the danger of carrying along the very small particals and getting also a high pressure drop. In the sense of this invention, partical size of one to two mm should be used because in this range it is still possible to have a tolerable pressure drop especially if the cross section of the adsorbent material is between one-half and one qm per thousand cbm hourly gas flow. The adsorbent layer should be at least one and one half meter long considering the high purity effect desired. The upper limit of this value depends on the allowable pressure drop and the amount of adsorbent in consideration of the incidental adsorption of the carrier gas.

If the gas is under pressure, whereby the effective volume of the gas under pressure is inversely proportional to the pressure, then in accordance with an additional thought of this invention, the volume relationship of 1:3-4 between raw gas and purge gas is assured when the pressure of the raw gas is at least three to four times higher than that of the purge gas. So, for example, if the standard volume, measuredate oneata., of raw gas and purge gas is the same, and the purge gas pressure is 1.1 ata., then a raw gas pressure of 3.3 to 4.4 ata. is sufficient

for the above-described relationship of 1:3-4 lower limit. If the degree of purity is not adequate, improvement can be obtained by increasing this ratio, or if this is not possible, through shortening of the cycle within the limits above, /so long as the loss of the carrier gas is still tolerable.

Should there not be enough purge gas available, then heating by a few degrees makes it possible under the given conditions to get away with still less purge gas. Halving the ratio of 3 would require an increase by 3 degrees C (lower limit) of the mean temperature level during the unloading as compared with the on-loading. Through this effective utilization of the purge gas and the doing away with large energy requirements to preheat it, one is compensating for the fact that the adsorbent quantity required has to be relatively large in consideration of its low loading. On the other hand, there is an advantage due to the large cross section of the adsorbent material/the pressure drop of the gas is smaller and the energy required to overcome the pressure drop is smaller. The general temperature level of the onloading and off-loading can vary with the ambient temperauter lower or higher. By shortening or lengthening the cycle, one can adjust to the varying conditions without any substantial changes required in the ratio of purge gas to raw gas. In order to work with considerably smaller adsorbent quantities, one can, in accordance with this invention, operate at lower temperature levels than ambient temperature, especially if the raw gas has to be cooled anyway for reasons of further fractionating.

14.

If the concentration of the component which is to be split off is high, one can build the adsorber towers into each other for the purposes of heat exchange. The adsorption heat then becomes an advantage in the off-loading process and desorption cooling becomes an advantage in the on-loading.

The heat exchange between the two processes would also be possible through a heat sink arrangement to which the effluent raw gas would give off its heat.

This heat would then be transferred to the purge gas upon cycling. The same means could be utilized in a case where the purge gas to begin with is cooler than the raw gas.

The heat of adsorption, which becomes available from the adsorption of larger vapor or gas masses, which gives a higher temperature to the adsorbent which is to be loaded, can, in accordance with this invention, be also utilized in that cycling occurs when a certain temperature has been reached at a certain point, for example, in the center of the adsorbent just being loaded. In this manner, the temperature increase of the adsorbent also remains available to assist the following partial off-loading.

The temperature rise can be used in such manner that the adsorber will switch itself, through a suitable arrangement. This can, for example, be accomplished through a contact thermometer which would be built into the adsorber and which through relays would close a circuit which would accomplish the switchover.

The process can be explained further on an example: Air with 0.03 percent CO<sub>2</sub> at pressure of 1.4 ata. and normal temperature is being passed through 2/parallel arranged adsorbers which are filled with charcoal of a length of 1.5 meters and a velocity of 600 cubic meters per cubic meters of adsorbent per hour. After ten minutes of on-loading time, the adsorber is being switched in known manner and following this the now loaded adsorber is being purged with CO<sub>2</sub> free nitrogen at 1.15 ata. at the same temperature and at a velocity of 2400 cbm per cbm adsorbent per hour. At the same time, the second adsorber which had been partially unloaded, while the first adsorber was previously being loaded, is now being loaded. The purity effect after 100 hours of cycling, is 99.5 percent corresponding to 0.00015 percent of CO<sub>2</sub> in the effluent gas.

The obtained advantages, as the example shows, lie in the high purifying effectiveness of the adsorbent which, in the foregoing example, was loaded only up to 20 percent of its equilibrium value, i.e., with 0.07 cubic meter CO<sub>2</sub> per gram of charcoal. This was accomplished by means of short cycling avoiding the adsorber becoming uneconomically big in size. When the raw gas contains a higher concentration of adsorbate, there is a special advantage in the short cycle time because practically the entire heat of adsorption remains in the adsorber and becomes available for the following desorption cycle. It is, therefore, possible to remove impurities in vapor form from gases also at lower pressure which otherwise would have been done at higher pressure (due to the relative lower vapor content) without imparing the purifying action and with little energy expenditure.

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Patent Claims:

- (1) A process to separate adsorbable components from a gaseous mixture by means of periodically cyclable, through adsorbate-free purge-gas-partially regenerated adsorbents, characterized in that the adsorbent is loaded only to less than 50 percent of its equilibrium load and less than 90 percent of its breakthrough load value, in which one then switches to the second container, which has been partially regenerated in the meantime, while the first container is being partially unloaded with unneeded purge gas in the opposite direction, whereby the cycle time is between five and thirty minutes.
- (2) A process in accordance with Claim 1 characterized in that the partial loading takes place at ambient temperature as well as at the same temperature as the partial unloading and whereby a purge gas volume is passed through the adsorbent of three to four times the effective raw gas volume.
- (3) A process in accordance with Claim 1 and 2 characterized in that one uses an adsorbent material of high selective capacity for the to be separated component.
- (4) A process in accordance with Claims 1 through 3 characterized in that one uses adsorbent material with particle size between 1 and 2 mm.
- (5) A process in accordance with Claim 1 through 4 characterized in that one uses an adsorbent material layer with a cross-section of from one-half to one qm per thousand cbm hourly flowing gas of at least a length of 1-1/2 meters.
- (6) A process in accordance with Claims 1 through 5 characterized in that when one has the same standard volume of raw and purged gas, the raw gas pressure is 5 to 4 times higher than the purged gas pressure.
- (7) A process in accordance with Claims 1 through 6 characterized in that when there is a lesser ratio between raw gas and purge gas than 1: 3 to 4, one uses a temperature of three degress higher purge gas for each halving of the ratio (lower limit).
- (8) A process in accordance with Claims 1 through 7 characterized in that one can lower the temperature level of the adsorption and desorption in relation to the ambient temperature.

- (9) A process in accordance with Claims 1 through 5 characterized in that, in accordance with known practice in the interest of heat exchange between loading and unloading, process (at higher concentration of the separable components); one builds the adsorbed vessels into one another in the form of a heat exchanger to obtain thermic contact with each other.
- (10). A process in accordance with Claim's 1 through 9 characterized in that one cycles the adsorbers automatically as soon as a certain temperature has been reached in the adsorbent caused by the adsorbing of larger gas and vapor quantities.

References: German Patent No. 624912

German Patent No. 704073; Bratzler; "Adsorption of Gases and Vapors," 1944, Pages 107, 108, and 121.

## DEFENDANTS' EXHIBIT M(5)

22. Kahle, H. "Die 'reversible' Adsorption als Mittel zur Vorreinigung und Zerlegung von Gasgemischen," Chemie-Ing.-Techn. 25 Jahrg. 1953/Nr. 3, pp. 144-48 and translation.

## Die "reversible" Adsorption als Mittel zur Vorreinigung und Zerlegung von Gasgemischen

Von Dr.-Ing. HEINRICH KAHLE, Gesellschalt für Linde's Elsmaschinen AG., Hölltiegelskreuth

An Hand von Diagrammen und schematischen Ausführungsbeispielen werden Grundlagen sowie apparative und verfahrensmößige Voraussetzungen für eine annähernd reversible Gasreinigung und Trennung durch Adsorption zwecks extremer Reinigung des behandelten Gases erläutert. Die Voraussetzungen sind: Kombination von Adsorbern mit Wärmeaustauschern an beiden Enden des Adsorbers, Be- und Entladungsbegrenzung des Adsorbers sowie Gegenstromentladung mit adsorbatfreien Spülgasen.

Streng reversible Prozesse sin! in der Technik weder bekannt, nech erscheinen sie realisierbar. Es gibt aber einige Verfahren, insbesondere in der Gaszerlegungstechnik bei tiefen Temperaturen, die sich einer "reversiblen" Arbeitsweise nähern. Dabei sei als "reversibel" eine Arbeitsweise bezeichnet, die einen technisch derzeit möglichen maximalen Wirkungsgrad besitzt oder sich ihm nähert. (Dieser ist seinerseits wiederum ein Teil dessen, was bei theoretisch reversiblen Arbeitsvorgängen erreicht werden könnte.) Der Vorgang der Erwärmung und Wiederabkühlung eines Gases kann als nahezu "reversibel" bezeichnet werden, wenn er mit Hilfe eines Gegenstromwärmeaustauschers mit möglichst geringer Temperaturdifferenz durchgeführt wird.

Auch für den Stoffaustausch sind derartige Arbeitsweisen bekannt geworden. Z. B. stellt die Rektifikation eine der Reversibilität sich nähernde Arbeitsweise bei der Stofftrennung dar. In dieser Hinsicht bemerkenswert sind auch Verfahren, bei denen die Lösungswärme des Waschvorganges für die Zwecke der mit Wämeaufnahme einhergehenden Entgasung des beladenen Waschmittels bei geringer mittlerer Temperaturdifferenz zwischen beiden Vorgängen nutzbar verwendet wird. Oft werden dabei erhebliche Temperaturbereiche durchlaufen, z. B. wendie Lösungsvorgänge bei tiefem Temperaturniveau vor sich gehen. Die beiden Vorgänge des Energie- und Stoffaustausches gehen hierbei parallel.

#### Energie- und Stoffaustausch in Regeneratoren

Energie- und Stoffaustausch kann auch in Regeneratoren bei richtiger Bemessung derselben und der Umschaltzeiten selbst über große Temperaturdifferenzen hinweg weitgehend reversibel durchgeführt werden, besonders wenn die auzutauschenden Stoffmengen in mößiger Konzentration-vorliegen.

Es sei das Beispiel des Kälteaustausches mit gleichzeitigem Stoffaustausch zwischen Rohgas und Spülgas in Kälteregeneratoren erwähnt.

Bild 1 zeigt eine übliche Regeneratorenanordnung in einem Zerlegungsannarat mit zwei gleichen, periodisch und regelmäßig umgeschatteten, mit Speichermasse gefüllten Regeneratorenästen nebst den zugehörigen Schaltorganen, deren Wirkungsweise schematisch dargestellt ist. Der Betriebszustand vor Umschaltung ist durch ausgezogene Pfeile, der Betriebszustand nach der Umschaltung durch gestrichelte Pfeile angedeutet. Der am oheren und unteren, schematisch dargestellten insmaltorgan eingezeichnete Diagonalbalken verbindet nach Jeder Drehung um 90° die Eintritts- bzw. Austrittsleitungen für zu- und abströmendes Gas, jeweils mit dem anderen Ast der Einrichtung. Das Rohgas mit den kondensierbaren Verunreinigungen tritt bei der dargestellten Schaltung durch den linken Regenerator mit etwa 25°C ein, gibt seine kondensierbaren Anteile durch Kondensation an die in der Perlode vorher kaltgeblasene Spelchermasse ab und tritt als gereinigtes Gas mit tiefer Temperatur Iz. B. -150 °Cl über die obere Hmechallwarrichtung nue

um zum Zerlegungsapparat geführt zu werden. Gleichzeitig strömt reines Spülgas, z. B. ein Zerlegungsprodukt durch die obere Umschaltung in den rechten Speicher mit —155° ein und bei der unteren Umschaltung, beladen mit den Verunreinigungen, die es durch Verdunsten aufgenommen hat, mit etwa 20° aus.

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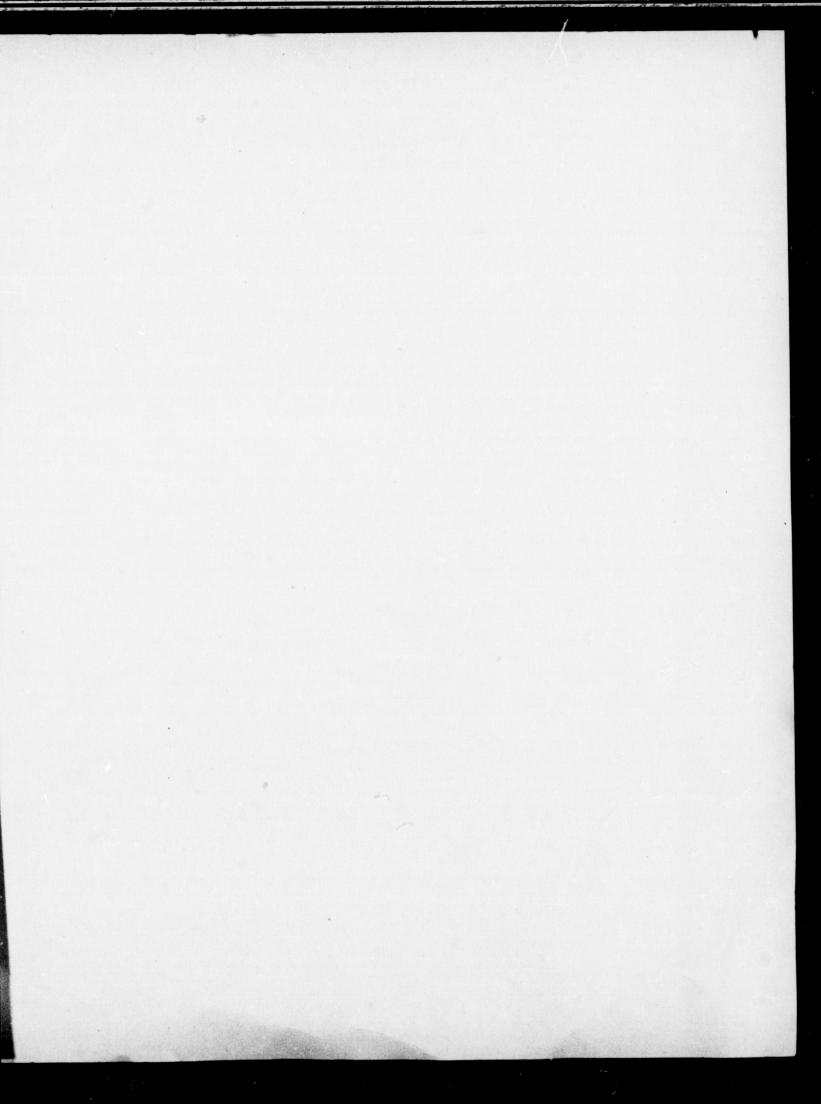
Bild 1. Schematische Darstellung des Regehersterhetriebes

Bild 1. Schematische Darstellung des Regehersterhetriebes

Betriebszustand vor Umschalten)

Auf der Meine Mei

Der Temperaturverlauf für ein Gasteilchen längs der Speichermasse im Regenerator, wie er sich im Beharrungszustand am Ende der Rohgasperiode bzw. am Ende der Spülgasperiode also kurz vor der Umschaltung einstellt. ist durch das Diagramm, Bild 2, im Prinzip dargestellt. Das kurz vor der Umschaltung auf die Schicht gelangende Gas ändert, wie ersichtlich, auf der Anfangsschicht der Speichermasse seine Temperatur zunächst nur wenig, da sich diese Schicht während der vorhergehenden Strömung des mit konstanter Temperatur eintretenden Gases bereits an dessen Temperatur angeglichen hat. Erst im weiteren Verlauf der Schicht fällt die Temperatur des Rohgases ab, bzw. steigt die des Spülgases an, Zu allen anderen Zeitpunkten, die zwischen zwei Umschaltungen liegen, verlaufen die Temperaturlinien der strömenden Gase zwischen der dick gestrichelten und der ausgezegenen Kurve, wobei jeweils senkrecht untereinanderliegende Punkte auf diesen beiden Kurven die belden Temperaturextreme in jedem Querschnitt der Speichermasse darstellen. Die Temperatur der Spelchermasse selbst bewegt sidi ebenfalls zwisdien jenen zwei Kurven. Ihr Temperaturmittel ist im Beharrungszustand konstant und ent-



zeiden des Regeneratorbetriebes ist dieses konstante Temperaturgefälle in der Speichermasse, das von Art und Menge der Masse sowie Temperaturzustand und Zusammensetzung des Rohgases und des Spülgases abhängig ist.

3.3

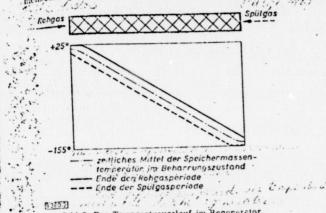


Bild 2. Der Temperaturverlauf im Regenerator

Enthält das Rohgas kondensierbare Bestandteile, so wird zu einem bestimmten Zeitpunkt, der vom jeweils herrschenden Betriebszustand abhängig ist, und in einem bestimmten Bereich der Speichermasse Kondensat aus dem Rohgas einerseits abgeschieden und in das Spülgas andererseits in einer im voraus zu berechnenden Menge yerdunstet; denn jeder Temperatur ist ein bestimmter Sättigungsdruck des kondensierten Anteils zugeordnet. In bestimmten Temperaturdifferentialen im Sättigungsgebiet wird stets ein bestimmter Betrag an Kondensat in dem "warm zu blasenden" Regenerator abgeschieden. bzw. in dem anderen "kalt zu blasenden" Regenerator verdunstet. Gleichzeitig wird einerseits ein bestimmter Betrag an Kondensationswärme frei bzw. andererseits gebunden. Diese positive bzw. negative Wärmetönung überlagert sich dem normalen Energieaustausch zwischen dem latenten Wärmeinhalt des Spülgasstromes einerseits und des Rohgasstromes andererseits über die Speichermasse als Zwischenträger, die sowohl die positive als auch die negative Wärmetönung zunächst speichert, um sie nach der Umschaltung an die andere Gasart abzugeben. Der Vorteil dieser Art des Energie- und Stoffaustausches gegenüber den üblichen Reinigungs- und Zerlegungsverfahren, bei denen die Kondensation aus einem mehrkomponentigen Gasgemisch oft in einem tieferen Temperaturniveau vorgenommen werden muß als die · Verdampfung, besteht darin, daß eine Verdunstung der Kondensate im Strom des Spülgases und der Zerlegungsprodukte in annähernd dem gleichen oder einem noch tieferen Temperaturniveau eintritt als die Kondensation, wodurch eine angenähert reversible Arbeitsweise erreicht wird.

Die bei der Kondensation frei werdende Wärme wird von den Speichermassen zwar im wesentlichen aufgenommen, Reste gehen jedoch mit dem Rohgasstrom in Zonen tieferer Temperatur. Auch die bei der Verdunstung frei werdende Kälte wird teilweise in Zonen höherer Temperatur getragen und trägt zur Vergrößerung der im Interesse des guten Wärmeaustausches möglichst klein zu haltenden Temperaturdifferenzen an den Wärmeaustauscher-Enden in unerwünschter Weise bei, vor allem wenn erheblichere Mengen von Kondensat abgeschieden und . wieder verdunstet werden.

### Energie- und Stoffaustausch in mit Regeneratoren kombinierten Adsorbern

Dem vorbeschriebenen Verfahren der Gasbehandlung in Regeneratoren sei ein solches in Adsorbern gegenübergestellt, wobei die Adsorber in bestimmter Weise mit Regeneratoren kombiniert und betrieben werden. Diese

Chemle-Ing.-Tedin. 25. Jabrg. 1953 / Nr. 3 Verfahren, welche eine interessante Parallele zu dem vorbeschriebenen Verfahren bilden, seien als Sorbogen-Verfahren bezeichnet. Eine Kombination ist in Bild 3 dargestellt').

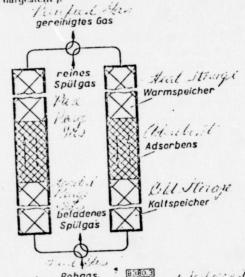


Bild 3. Schemanische Darstellung des mit Regeneratoren arbeitenden Sorbogen I-Verlahrens

### Sorbogen I - Verlahren

In der kombinierten zweiästigen Einrichtung, die mit Rohgas bzw. Spülgas von etwa gleicher Temperatur beschickt wird, und die sich für jeden Ast aus einem Kaltspeicher, dem Adsorber und dem Warmspeicher zusammensetzt, stellt sich ohne äußeres Zutun, lediglich unter dem Einfluß der positiven Wärmetönung des Adsorptionsvorganges und der negativen Wärmetönung des Desorptionsvorganges, das Temperaturgefälle im Adsorber derart ein, daß die Temperatur von der Eintrittsstelle des Rohgases zum Reingasaustritt ansteigt. Es ergibt sich hierbei ganz von selbst, daß der Speicher auf der Rohgasseite die Funktion eines Kaltspeichers, der Speicher auf der Reingasseite die Funktion eines Warmspeichers übernimmt.

An den freien Enden der Speicher herrschen nach Bild 4 je nach dem jeweiligen Betriebszustand der Einrichtung von der Umgebungstemperatur nur wenig verschiedene, in geringen Grenzen schwankende Temperaturen. Die Temperatur eines mit Umgebungstemperatur in den Kaltspeicher einströmenden Rohgasteilchens sinkt also zunächst im Kaltspeicher, steigt im Adsorbens wieder bis auf über Umgebungstemperatur an, um längs der Schicht des Warmspeichers wieder auf etwa Umgebungstemperatur abzusinken.

In Bild 4 ist der Temperaturverlauf der Gase in den beiden Asten jeweils kurz vor der Umschaltung dargestellt. Im Interesse der vereinfachten Darstellung wurde hier und in Bild 8 das Stück des konstanten Temperaturverlaufes fortgelassen (vgl. Bild 2).

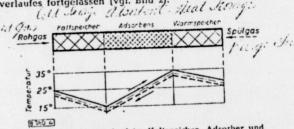


Bild 4. Temperaturverlauf im Kaltspeicher, Adsorber und

Warmspeicher beim Sorbogen I-Verfahren

Sorbogen I-Verfahren

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Darch regelmäßige Umschaltung in begrenzten Zeitraumen wird datur gesorgt, daß der Temperaturgradient sowch! im Adsorbens als auch in den Speichern autrecht erhalten bleibt. Das Spulgasteilchen, welches den jeweils beladenen Adsorber nach der Umschaltung entlädt, unterliegt, wie ersichtlich, umgekehrt wie das Rohgas, da es entgegengesetzt zu diesem strömt, zunächst einem Temperaturanstieg über dem Warmspeicher, anschließend einem Temperaturabfall entlang der Adsorbensschicht, um anschließend über dem Kaltspeicher am anderen Ende des Adsorbens wieder auf Umgebungstemperatur angewärmt zu werden.

Die bei der Bindung adsorbierbarer Bestandteile am Adsorbens freiwerdende Adsorptionswärme wird mit dem gereinigten Gas eine bestimmte Strecke in der Richtung der Strömung des Rohgases fortgetragen. Ein Teil der Wärme verbleibt auf dem Adsorbens selbst, da auch dieses ein gewisses Wärmespeichervermögen besitzt; der restliche Teil wird von der Speichermasse aufgenommen.

Umgekehrt werden bei der Entladung des Adsorbens entsprechende Kältebeträge frei bzw. Wärmebeträge gebunden, die teils aus der Adsorbensmasse selbst, teils aus dem Gas entnommen werden. Dabei kann die Temperatur wesentlich unter Umgebungstemperatur sinken. Die bei der Entladung erzeugte Kälte verbleibt nicht allein auf dem Adsorbens, sondern wird durch das Spülgas zum Teil auf den Kaltspeicher übertragen, in dem das mit Desorbat beladene Spülgas wieder auf etwa Umgebungstemperatur angewärmt wird.

Je größer die adsorbierten Beträge sind, um so größer ist nicht nur die Wärmeentwicklung bei der Adsorption, sondern auch die Kälteerzeugangs bei der Desorption. Die Speichermassen an den Enden der Adsorptionsschicht sorgen dafür, daß die Wärmetönung des Adsorptionsvorganges, die sonst z. B. durch Kühlwasser abgeführt und vernichtet werden mußte, nunmehr nutzbringend für den gegenläufigen Desorptionsvorgang, der bisher durch Heizung unterstützt wurde, zur Verfügung steht.

Ersetzt man die Speicher an den Adsorbens-Enden durch Röhren-Wärmeaustauscher, so wird die gleiche Wirkung erreicht. Die Umschaltorgane liegen in diesem Fall zwischen den kontinuierlich betriebenen Austauschern und den Adsorbern, Bild 5.

Die bereits früher vorgeschlagene Anordnung des Adsorbens in den Rohren des Wärmeaustauschers und die Durchführung von Adsorption und Desorption in diesen dürste die Wirksamkeit der obigen Anordnungen nicht ganz erreichen.

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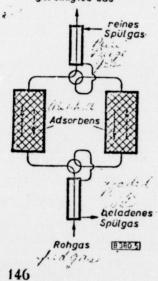


Bild 5 (links). Schematische Darstellung des mit Rohrenwärmeaustauschern arbeitenden Sorbogen I-Verfahrens Das Prinzip der Teilbeladung und Teilentladung

Daß dieser Vergang der Beladung und kattadung des Adsorbens auch bezüglich des Spulgasverbrauchs angenähert reversibel vor sich geht und gleichzeitig hohe Reinigungseffekte erzielt werden, kann durch zwei Arbeitsprinzipien bei der Beladung bzw. Entladung des Adsorbens erreicht werden. Sie seien hier als die Prinzipien der Teilbeladung und Teilentladung bezeichnet<sup>2</sup>).

Daß im einströmenden Rohgas das Adsorbens nicht bis zur Sättigung sondern nur bis zum sogenannten Durchbruchswert (d. h. dem Beladungswert des Adsorbens, bei dem die zu entfernende Komponente des strömenden Gases im austretenden gereinigten Gas erscheint) beladen wird, ist bereits seit längem allgemein bekannt. Will man jedoch hohe Reinheitswerte erreichen, so ist die Beladung des Adsorbens bis in die Nähe des Durchbruchswertes noch zu hoch.

Nach dem neuen Prinzip der Teilbeladung wird das Adsorbens nur bis zu einem Bruchteil des Durchbruchswertes beladen und die Beladung dann abgebrochen. Auf diese Weise bleibt eine relativ große Adsorbensschicht völlig unbeladen, was hingenommen werden kann, da die Eigenart des geschilderten Verfahrens und der Anordnung eine häufigere Umschaltung gestattet.

Durch Anwendung dieses Prinzips wurden in einer technischen Anlage, wie später beschrieben, erstäunlich hohe Reinigungseffekte bei Luft auch von verhältnismäßig schlecht adsorbierbaren Verunreinigungen wie CO2 bei einer Temperatur erreicht, die man bisher als ungeeignet für diesen Zweck angesehen hat, zumal, wenn gleichzeitig von einer Erhitzung des Spülgases völlig abgeschen wird und das noch zu beschreibende Arbeitsprinzip der Teilentladung angewendet werden soll. Voraussetzung für den höchsten Reinigungseffekt ist selbstverständlich, daß das Spülgas von den zu entfernenden Bestandteilen völlig frei ist und stets in derselben, zur Rohgasströmung entgegengesetzten Richtung über das Adsorbens strömt. Das Prinzip der Teilentladung gründet sich auf die Überlegung, daß eine vollständige Entladung des Adsorbens einen zu hohen Spülgasaufwand erfordert, um es für die nachfolgende Periode der Beladung möglichst aufnahmebegierig zu machen.

Die beiden Arbeitsprinzipien seien durch Bild 6 erläutert, das sich auf Messungen gründet, die vor einiger Zeit im Laboratorium der Gesellschaft für Linde's Eismaschinen ausgeführt wurden, und über die später berichtet werden soll. Dabei wurde gefunden, daß man die bei Umgebungstemperatur (etwa 20°) über eine 1,5 m lange Schicht einer sog. Carbotoxkohle von 1 bis 2 mm Körnung geführte Luft von ihren Verunreinigungen u. a. auch von der schwer adsorbierbaren Kohlensäure mit einem Reinigungseffekt von erheblich über 99% entfernen konnte, wenn man, ausgehend von einer CO,-Restbeladung von etwa 8% des Sättigungswertes, die Kohle bis zu einem Wert von etwa 25% des Sättigungswertes belud und dann anschließend bei etwa gleicher Temperatur mit etwa der dreifachen Menge Spulgas im Gegenstrom bis auf den Restwert von etwa 8% wieder teilentlud.

In Bild 6 ist auf der Abszisse die Schichtlänge in Bruchteilen der Gesamtschichtlänge, auf der Ordinate die relative "Belädungshöhe" im vertikalen Querschnitt der

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live	"Beladungshöhe" im vertika	len Querschnitt der
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Schient (das Adsorbens ist liegend gedacht) in Bruchteilen der maximalen (Sättigungs-) Beladung aufgetragen. Die beiden S-förmigen Linien sind die Beladungsfronten, welche die sog. Zuladungszone Z., (einfach schrattiert) ein-Clieffen. Die linke Front begrenzt die Zone der dauernden Beladung bzw. Restladung (R doppelt schraffiert), die schte Front die Zone der Zuladung im Augenblick der Umschaltung auf Gegenstromentladung. Zwischen dieser rechten S-formigen Beladungsfront und dem Schichtende liegt die unbeladene Zone. Über diese und ähnliche Messungen wird in einer späteren Arbeit berichtet werden.

Dadurch, daß im Gegenstrom zum Rohgas über das zu entladende Adsorbens strömendes Spülgas zum Schlusse die ständig im Sättigungszustand befindliche Adsorbensschicht bespült, kann sich das Spulgas bis zum Schluß der Spülgasperiode mit einem Maximum an desorbierten Bestandteilen aufladen. Die Spülung wird beendet, wenn die Aufladung des Spülgases wesentlich absinkt. Man kann bei isothermer Teilbeladung und Entladung bei gleichem Gesamtdruck mit etwa dem drei-· fadien Spulgasvolumen redinen, wenn man gleichzeitig , löchsten Reinigungseffekt verlangt. Mit zweifacher Spülgasmenge sinkt der Reinigungseffekt etwas ab. Bei je 5°C höherer Spülgastemperatur erniedrigt sich das Verhältnis des Spülgas- zum Rohgasvolumen jeweils auf die Hälfte, so daß man bei einer um 10° höheren Temperatur bereits weniger Spülgas als Rohgas benötigt3).

Es ist Sache der Planung, die Forderung, das vorhandene Spülgas gut auszunützen, mit der Forderung nach gutem Wärmeaustausch in Einklang zu bringen. Es ist jederzeit möglich, die angegebenen Richtwerte um Bruchteile zu überschreiten, so daß beiden Forderungen, die sich nicht widersprechen, leicht gerecht zu werden ist.

Der Umstand, daß man bei isothermer Entladung ein Mehrfaches des Rohgasvolumens an Spülgas benötigt, zeigt, daß man trotz dieser sparsamen Arbeitsweise doch mit einer gewissen Hysterese rechnen muß. Abgeschen davon, daß man völlige Gleichgewichtseinstellung zwischen adsorbierter Phase und Gasphase nicht erwarten kann, hängt der Mehrverbrauch an Spülgas mit der Temperatursenkung zusammen, die sich bei der Entladung des Adsorbens in der zuleizt gespülten noch verhältnismäßig hoch beladenen Adsorbensschicht einstellt. Im Labormaßstab, d. h. bei großer Oberfläche im Verhältnis zur Masse und guter Wärmeab- bzw. Zustrahlung ist die-

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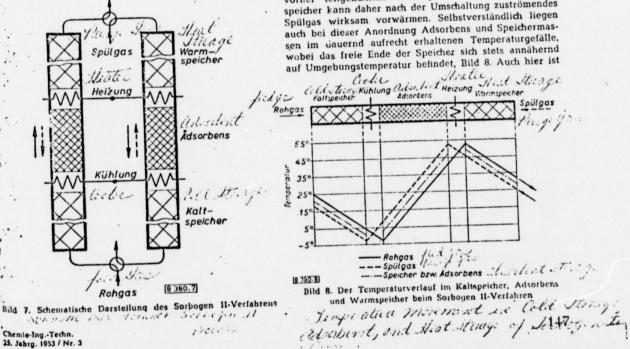
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ser Effekt kaum merklich, bei einer technischen Anlage konnte er jedoch deutlich beobachtet werden. Die Anordnung der Speichermassen an den Enden der Adsorbensschicht bedingt es, daß sich dieser Effekt nicht ungünstiger auswirkt. Als Folge der Anwendung des Teilentladungsprinzips läßt die im Adsorbens noch vorhandene Restbeladung langs der Restbeladungsfront die Adsorptionswärme während der Beladung nicht auf einem räumlich engen Bereich, sondern auf eine größere Strecke verteilt frei werden, wodurch der bereits oben erwähnte Temperaturanstieg gegen das Adsorbens-Ende hin und ein besserer thermischer Wirkungsgrad erzielt wird. In einem völlig entladenen Adsorbens würden dagegen auf kleinem Raum große Wärmemengen frei werden, was vom Standpunkt des reversiblen Arbeitens gesehen besonders dann ungünstig ist, wenn wie bei dem Sorbogen II-Verfahren, Bild 74), aus besonderen Gründen der Temperaturgradient längs der Adsorbensschicht durch Heizbzw. Kühleinrichtungen zwischen Austauschern und Adsorbern vergrößert wird, um etwa flüchtigere Verunreinigungen bzw. Gasbestandteile zu binden und evtl. anzureichern.

### Sorbogen II - Verfahren

Hierbei werden eine Kühleinrichtung am Rohgaseintrittsende, z. B. zwischen Kaltspeicher und Adsorbens, bzw. eine Heizeinrichtung am Reingasaustrittsende, z.B. zwischen Warmspeicher und Adsorbens, angeordnet. Diese Einrichtungen erlauben, Heizung und Kühlung in beiden Asten gleichzeitig und ständig zu betreiben. Dadurch wird Zeit gewonnen für das Vorkühlen bzw. Vorerhitzen der Speichermassen, die das Rohgas vorkühlen bzw. das Spülgas voreihitzen sollen. Die gegenseitige Beeinflussung von Heiz- und Kühleinrichtung wird durch die regelmäßige Umschaltung und die ständige Aufrechterhaltung eines Temperaturgefälles längs der Adsorbensschicht verhindert. Je nach dem Strömungszustand in der gerade herrschenden Schaltperiode kühlt die Kühleinrichtung entweder das Rohgas vor seinem Eintritt in das Adsorbens oder nach Umschaltung das austretende beladene Spülgas vor dessen Eintritt in den Kaltspeicher, der nun nach vorübergehender Teilanwärmung durch Rohgas wieder teilweise kaltgeblasen wird, Bild 7. Die Heizeinrichtung erhitzt in einer Periode das über dem Warmspeicher vorgewärmte Spülgas, bevor es auf das Adsorbens trifft. In der darauf folgenden Periode erhitzt sie das gereinigte Gas, bevor es auf den anschließenden, vorher teilgekühlten Warmspeicher trifft. Der Warmspeicher kann daher nach der Umschaltung zuströmendes



wiederum die Anderung der Temperatur eines durch die Einrichtung strömenden Rol:gas- bzw. Spulgasteilchens kurz vor der Umschaltung schematisch dargestellt. Unter dem Einfluß von Heizung und Kühlung überschneiden sich die Temperaturlinien von Roh- und Spulgas. Durch die strichpunktierte Linie ist wieder der Verlauf der Mitteltemperatur des Adsorbens bzw. der Speichermasse dargestellt. Günstig ist bei dieser Anordnung die Verstärkung des Heizungseffektes durch die gegen das Adsorbens-Ende getragene Adsorptionswärme und die Verstärkung des Effektes der Kühleinrichtung durch die gegen den Adsorbens-Anfang getragene Desorptionskalte. Auch diese Anordnung läßt eine angenähert reversible Arbeitsweise bis in Gebiete weit gesenkter Temperatur bei entsprechend großem Temperaturgefälle zu. Wie bereits oben erwähnt, ist ein Uberschuß des Spülgasvolumens über das Rohgasvolumen bereits bei 10°C Temperaturerhöhung des Spülgases nicht mehr erforderlich.

Will man die adsorbierten Gasbestandteile wieder gewinnen, so genügt eine weitere Erhöhung der Temperaturdifferenz mit gleichzeitiger Verminderung der Spülgasmenge. Eine weitere Möglichkeit der Anreicherung besteht in der Desorption bei Unterdruck zweckmäßig und im Sinne der obigen Ausführungen unter Beibehaltung der Gegenstromspülung. Als Spülgas kann unter diesen Umständen auch ein vom gereinigten Gas hinter dem Adsorbens abgezweigter Teilstrom verwendet werden. Die Anwendung eines mäßig, z.B. auf 2 b.s 10 atü erhöhten Druckes bei der Beladung des Adsorbens ist günstig, falls das gereinigte Gas unter Druck zur Verfügung stehen soll. Bei höheren Drucken steigen die Gasverluste beim Umschalten u. U. über einen zulässigen Wert, da auch ein Teil des gereinigten Gases adsorbiert wird und bei der Druckentlastung beim Umschalten verlorengeht. Über die technische Anwendung des Sorbogen I-Verfahrens sowie die vorbereitenden Versuche dazu soll in einer anschließenden, späteren Arbeit berichtet werden.

#### Zusammenfassung

Die verfahrensmäßigen und apparativen Voraussetzungen für eine angenähert reversible Arbeitsweise (als Sorbogen I-Verfahren bezeichnet) bei der Reimgung von Gasen durch Adsorption bei verhältnismäßig kurzfristigem Wechsel der Adsorber vorzugsweise für die Zwecke einer weiteren Zerlegung des reinen Gases unter erhöhtem Druck und bei erniedrigter Temperatur werden erläutert. Das Verfahren wird infolge der Ahnlichkeit des Umschaltbetriebes sowie thermischer und stoffaustauschmäßiger Eigentümlichkeiten mit dem Verfahren der Gasreinigung durch Kälteregeneratoren verglichen.

An Hand von Schemazeichnungen und Diagrammen werden die Prinzipien des "reversiblen" Arbeitens, nämlich Wärmeaustausch zwischen Adsorptions- (Belade-) und Desorptions- (Entlade-)vorgang auch ohne Anwendung von fremden Heiz- und Kuhlquellen erläutert. Eine Bedingung, um einen höchsten Reinigungseffekt auch bei der Entfernung schwer adsorbierbarer Verunreinigungen zu erreichen, ist die Aufrechterhaltung einer sehr großen freien (unbeladenen) Zone; dies wird als das Prinzip der "Teilbeladung" bezeichnet. Eine "reversible" Arbeitsweise wird durch Anwendung des Prinzips der "Teilentladung" gefördert. Die bekannte und folgerichtig stets angewandte Spülentgasung mit reinem Spülgas im Gegenstrom zum Rohgas ist eine weitere Voraussetzung sowohl für höchsten Reinigungseffekt als auch "reversibles" Arbeiten. Die Arbeitsweise für eine Anreicherung und Gewinnung adsorbierbarer Bestandteile (als Sorbogen II-Verfahren bezeichnet) unter Anwendung der gleichen Prinzipien und unter sparsamster Verwendung von Energie für Heizung und Kühlung nebst den apparativen Voraussetzungen hierfür wird angegeben.

Eingeg. 11. Aug. 1952 [B 380]

- Disch, Patentanm. G 6724 IV b/12e. C 2, Disch. Patentanm. p 22 720 IV b/12eD. C 20 Disch. Patentanm. G 405 IV b/12e.
- Dtsch. Patentanm. G 94 IV b, 12e.

# BERICHTE AUS DER CHEMUSCHEN TECHNAR

# Versammlungsberichte

### Vortragstagung "Hochtemperaturtechnik" am 10. Oktober 1952 in Essen

Der Arbeitsausschuß "Hochtemperaturtechnik" im Fachausschuß Verfahrenstechnik des VDI trat am 10. Oktober 1952 zum ersten Mal mit einer Vortragstagung an die Offentlichkeit, nachdem er bisher über seine Arbeitssitzungen nur Kurzberichte veröffentlicht hatte')2). Sie fand gemeineam mit dem Haus der Technik e. V., Essen, statt. Prof. Dr.-Ing. habil. K. Krekeler begrußte die Versammlung, vor allem die ausländischen Gäste. Dir. Dr.-Ing. E. h. K. Rieß legte als Obmann des Fachausschusses die Gründe dar, die vor einigen Jahren zur Schaffung des Arbeitsausschusses geführt hatten, obwohl schon der Industricofen-Ausschuß beim Verein deutscher Maschinenbau-Anstalten und verschiedene einschlägige Ausschüsse beim Verein deutscher Elsenhüttenleute bestanden. Er befaßt sich mit Problemen auf folgenden Gebieten:

- 1. Physikalisch technische Grundlagen (Warmeübergang, Strömungsfragen, Fragen der Oberflächenreaktionen u. a.),
- 2. Verbrennungs-, Vergasungs- und Entgasungstechnik (Gaserzeugung, Gas-, Kohlenstaub- und Olbrenner, Carburierung).
- (konstruktiv, mit Wärmerückgewinnung),
- 4. Baustoff-Fragen,

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5. Meß- und Regeltechnik, deren Entwicklung selbst jedoch in den Händen des Normenausschusses für Me3- und Regeltechnik liegt.

In enger Beziehung zu den interesslerten Kreisen der Praxis soll der Ausschuß die dringlichsten Aufgaben herausstellen, sie an die richtigen Stellen zur Bearbeitung leiten und sie finan-zieren helfen. Wertvolle Hilfe wird hierbei das neue Institut für Verfahrenstechnik in Aachen leisten können.

Zum Abschluß teilte Dr. Rieß - mit Worten des Dankes für die geleistete Arbeit - mit, daß Prof. Joh. Körting aus Gesundheitsrücksichten sein Amt als Obmann niedergelegt und Dr.-Ing. A. Schack es übernommen habe; dann übergab er die Leitung der Tagung an Prof. Dr.-Ing. F. Schuster.

Prof. Dr.-Ing. E. SCHWARZ VON BERGKAMPF, Leobent Rationelle Modellhetrachtungen von Industrie Ofen')

Die Untersuchungen haben zum Ziel, an Hand von dimensionslosen Kenngrößen, wie der Reynolds, Grashof- und Nußeltschen Zahl, die Übertragung von Modellgrößen auf große Bctriebsausführungen von Ofen zu ermöglichen. Die Ergebnisse der durchgeführten Rechnungen stimmten überraschend gut überein mit einer großen Zahl von Ausführungen der verschiedensten Ofen, wie Schachtöfen (Hochöfen, Kupolofen, Katkofen usw.), Herdöfen mit flüssigem und festem Gut sowie Drehofen. Die vom Redner eingeführten Vergrößerungsexponenten geben dem Ofenbauer wertvollen Anhalt bet seinen Berechnungen.

(Some Chare Ingenieve Lectrick As you of patricular, 1455 Hord)

# THE "REVERSIBLE" ADSORPTION AS A MEANS FOR PRECLEANING

# AND FRACTIONATING OF GASEOUS MIXTURES

by Dr. -Ing. Heinrich Kahle, Gessellschaft für Linde's Eismachinen AG., Hollriegelskreuth

On hand of diagrams and schematic layout examples, the principles as well as the equipment and process foundations for an approximate reversible gas cleaning and separation through adsorption for the purpose of extreme purification of the process as are explained.
The requisits are: combination of adsorbers with heat exchangers at both ends of the adsorbers, loading and unloading limitation of the adsorbers as well as counter flow unloading with adsorbate-free purge gases.

Strictly reversible processes are neither known in the technique nor do they appear attainable. But there are some processes, particularly in the fractionating technique of gases at low temperatures which come close to a reversible operation. In this respect, a reversible operation shall be defined as one that has a technical maximum efficiency or approaches it. (This in turn is a part of what could be obtained in the existing a part of what is a part of which are the existing a part of which are the existing a part of which a part of which are the existing a part of be obtained in theoritical reversible work operations.) The operation of heating and re-cooling of gases can be called nearly "reversible" if it is done with the help of the counter flow heat exchanger with lowest possible temperature differential.

Also in the exchange of matter have such operating methods become known. For example, fractionating is an operating method that is approaching reversibility in the separation of matter. In this respect, worth noting are also processes where the heat of solution of the washing operation is used for the heat intake needed in the degasing of the loaded washing means at a small mean temperature differential between the two processes. Often considerable temperature spans are covered, i.e. when the solution processes are taking place at low temperature levels. The two operations of the energy and matter exchange are running parallel in this case.

# Energy and Matter Exchange in Regenerators

Energy and matter exchange can be reversibly accomplished to a large degree even over great temperature differentials with proper sizing and time cycling, especially when the to-be-exchanged quantities of matter are in moderate concentration.

An example is the cold temperature exchange concurrent with the exchange of matter between raw gas and purged gas in a cold · temperature regenerator.

Picture 1 shows the usual regenerator arrangement of a fractionating apparatus with two equal, periodically and regularly cycled with storage mass filled regenerator branches, together with the cycling components whose operation is schematically shown. The operating condition before cycling is shown by the solid acrows, the operating condition after cycling by the dashed arrows. The diagonal bar drawn into the upper and lower schematically shown cycling component connect after every 90° rotation the inlet respectively the outlet lines for the in and out going gas, each time with the other branch of the apparatus. The raw gas with the condensible impurities enters the left regenerator at about 25° C in the illustrated cycle, gives off its condensible parts through condensation to the storage which had been cooled before and leaves through the upper cycling component as clean gas with low temperature (i.e., minus 150° C) to be passed on to the fractionating apparatus. At the same time, clean purged gas, i.e., a fractionating apparatus. At the same time, clean purged gas, i.e., a fractionation product, flows through the upper cycle component into the right storage at minus 155° and flows out at the lower cycling component at about 20° loaded with the impurities which it collected through evaporation. The temperature course of a particle of the gas along the storage mass in the regenerat as it adjusts itself in its steady condition at the end of the raw gas period respectively at the end of the purge gas period, in other words shortly before the cycling, is shown in principle by a diagram in Picture 2.

The gas that reaches the storage mass shortly before the cycling changes its temperature initially only very little at the beginning layer of the storage mass, because this layer has already adjusted its temperature during the prior inflow to that of the constant temperature of the incoming gas. Only further down the mass the temperature of the raw gas falls off, respectively that of the purge gas climbs. At all other times, between the two cycles, the temperature lines of the flowing gas stay between the fat dashed and solid lines, whereby the points lying on both curves vertically below and above one another represent the two temperature extremes at any cross section of the storage mass. The temperature of the storage mass itself moves also between these two curves. Its mean temperature is constantly in the steady condition, corresponds to the dot-dash curve. One characteristic of the regenerator operation is this constant temperature slope in the storage mass which is dependent upon the type and quantity of the mass as well as the temperature condition and the composition of the raw and purge gases.

If the raw gas contains condensible components then at a given point in time, which depends on respective operating conditions, and in a certain area of the storage mass condensate will be separated from the raw gas on one hand and on the other hand evaporated into the purge gas in a quantity that can be calculated in advance, because to each temperature belongs a specific saturation pressure of the condensible part. At specific temperature differentials in the area of saturation a certain amount of condensate will always be knocked out in the "to-be-warmed" regenerator; respectively will be evaporated in the "to-be-cooled" regenerator. At the same time a given amount of condensation heat is released on one hand respectively required

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on the other hand. This positive respectivley negative, temperature tint superimposes itself on the normal energy exchange between the latent temperature content of the purge gas on one side and the raw gas on the other side, with the storage mass as the exchange medium, which stores the positive as well as the negative temperature tint initially, to pass it on to the other gas type after cycling. The advantage of this kind of energy and matter exchange, compared with the usual cleaning and fractionating processes where the condensation of a multicomponent gaseous mixture often has to take place at a lower temperature than the evaporation, is that the evaporation of the condensate in the stream of the purge gas and the fractionation products occurs at about the same or even at a lower temperature level than the condensation, whereby an approximate reversible operation is achieved.

The heat which is released during condensation is substantially taken up by the storage masses, however, remainders pass with the raw gas to zones of lower temperature. Also the cold that is being released during evaporation is carried in part to zones of higher temperature and contributes undesirably to the increase in the temperature differential at the extremes of the heat exchanger which (the temperature differential) in the interest of good heat exchange should be kept as small as possible. This happens particularly when considerable quantities of condensate are knocked out and are again evaporated.

# xchange of Energy and Matter in Adsorbers Combined with Regenerators

The previously described process of gas treatment in regenerators is now compared with one in adsorbers, whereby the adsorbers are combined with the regenerators and are operated in a certain manner. These processes which are an interesting parallel to the prior described process shall be identified as Sorbogen Processes. A combination is shown in Picture 3.

### Sorbogen 1 Process

In the combined two-branch apparatus which has an inflow of raw gas, respectively purge gas, of about the same temperature and which consists in each branch of a cold storage, the adsorber, and the heat storage, without external influence, so'lely due to the positive temperature tint of the adsorption process and the negative temperature tint of the desorption process, the temperature curve in the adsorber establishes itself so that the temperature from the inlet point of the raw gas to the outlet point increases. From this it is self-evident that the storage at the raw gas side has taken on the function and a cold storage; the storage on the clean gas side, the function of a heat storage.

Per Picture 4, at the free end of the storages, temperatures d'fer onlyslightlyfrom the surrounding temperatures and vary only i close limits. The temperature of the particle of raw gas flowing at ambient temperature into the cold storage therefore initially

drops in the cold storage, rises again above the ambient temperature in the adsorber, to be cooled down again to the ambient temperature along the layers of the heat storage.

In Picture 4, the temperature course of the gases in the two branches just before cycling is shown. For simplicity sake here and in Picture 8, the part of the constant temperature curve was left off (see Picture 2).

Through regular cycling, within certain time limits, one assures that the temperature gradient is maintained in the adsorbers as well as in the storages. The particle of purge gas which desorbs the adsorber after cycling is subject, as evident, contrary to the raw gas to which it flows in opposite direction, first to a temperature rise at the heat storage, then a temperature drop along the layers of the adsorber, followed by a warming to ambient temperature at the cold storage at the other end of the adsorber.

The adsorption heat that is released during the binding of adsorbable components is carried along a certain stretch by the clean gas in the direction of the flow of the raw gas. A part of the heat remains on the adsorbent itself, as it also has a certain heat storage capacity: the rest is taken up by the storage mass.

Vice versa during desorption of the adsorbent corresponding cold quantities are set free, respectively, heat is being bound which is taken in part from the adsorbent mass and in part from the gas itself. Thereby the temperature can sink considerably below the ambient. The cold produced during desorption does not remain entirely on the adsorbent, but is carried in part to the cold storage by the purge gas, where the purge gas, which is loaded with desorbate, is again brought up to the ambient temperature.

The larger the adsorbed quantities, the larger is not only the development of heat during adsorption, but also the cold production during desorption. The storage masses at the end of the adsorption layers take care that the heat tint of the adsorption process which otherwise would have to be carried away by cooling water and eliminated, for example, is now usefully available to the opposite desorption process, which up to now was supported by heating.

If one replaces at each end of the adsorbers, the storage with tubular heat exchangers, one accomplishes the same thing. In this case, the cycling components are located between the continuously operating exchangers and the adsorbers, Picture 5.

The previously proposed arrangement of the adsorbent in the pipes of the heat exchanger and the adsorbing and desorbing therein is not likely to have the effectiveness of the above arrangement.

# The Principle of Partial Loading and Partial Unloading

That this process of loading and unloading of the adsorbent can also be approximately reversible regards the purge gas consumption and at the same time, achieves a high degree of purity, can be attained through two operation principles in the adsorption respectively desorption of the adsorbent. Let us call them here, the principle of partial loading and partial unloading.

That with the inflowing raw gas, the adsorbent is not loaded to saturation, but only to a breakthrough value, has been known for a long time. (Breakthrough value is the loading value of the adsorbent at which the component that is to be removed from the inflowing gas, appears in the outgoing clean gas.) If one, however, wishes to obtain a high degree of purity, the loading of the adsorbent to nearly its breakthrough value is still too high.

In accordance with the new principle of partial loading, the adsorbent is only loaded to a fraction of its breakthrough value and the adsorption is then interrupted. In this way a relatively large layer of the adsorbent remains entirely unloaded, which is acceptable, as it is the characteristic of the described process and arrangement to allow a more frequent cycling.

Through application of this principle, surprisingly high purity of air was achieved in a technical installation, as later described, also with relatively difficult adsorbable impurities like CO2, at a temperature, which up to now was considered unsuitable for this purpose, additionally when at the same time the heating of purge gas was omitted and the still to be described principle of partial desorption was utilized. Requisite for the highest degree of purity is, of course, that the purge gas be entirely free of the components to be removed and always flows in the same direction over the adsorbent which is opposite to the raw gas flow. The principle of partial desorption (unloading) is based on the consideration that a complete unloading of the adsorbent would require too large a quantity of purge gas to make it most eager for the following period of adsorption.

The working principles are explained in Picture 6, which is based on measurements performed some time ago in the laboratories of the Gessellschaft fur Linde's Eismaschinen and about which will be reported later. It was found that at an ambient temperature (20°C) one could clean air of its impurities, among others also of the with difficulty adsorbable carbon dioxide, with a purity in excess of 90%, using a layer of 1.5 m of activated charxoal. I to 2 mm of grain, starting with a CO<sub>2</sub> residual loading of 8% of the saturation value, then loading the charcoal to about 25% of its saturation value, and then subsequently, at about the same temperature, purging with a volume of about three times of purge gas in counterflow to the residual value of about 8% partially unloaded.

Picture 6 shows on the absissa, the length of the layer in fraction of the whole, and on the ordinate, the relative loading height of the vertical cross section (the adsorbent is pictured as lying horizontally) in fraction of maximum saturation loading. The two S forming lines are the loading fronts which are enclosing the so-called add-load zone Z. The left front definiates the area of the permanent load, respectively residual load, the right front, the one of the add-load at the moment of cycling to the counterflow unloa ing. Between this S forming load front on the right and the end of the layer lies the unloaded zone. This and similar measurements will be reported in a later article. Because the purge gas in counterflow to the raw gas streams at the end over the adsorbent layer which is constantly saturated, it loads itself up with desorbable components to the maximum until the close of the purge gas period. The purg ag is stopped when the loading of the purge gas drops off substantia ly. One can figure an isotherm partial adsorption and desorption at the same total pressure with about three times the purge gas volume if one wants, at the same time, maximum cleaning effect. With twice the purge gas volume, the cleaning effect drops off some. At each 5°C higher purge gas temperature, the ratio of purge gas to raw gas volume is cut in half, so that at 10°C higher temperature one already needs less purge gas than raw gas. It is a matter of planning to coordinate the requirement for a good heat exchange. It is a always ossible to exceed the guide figures by fractions, so that one can do justice to both requirements which do not contradict each other.

The situation that with isotherm desorption, one needs several times the purge gas than the raw gas volume, in spite of this economical working method, shows that one has to figure with a certain hysteresis. Apart from the fact that one cannot expect complete equilibrium between adsorption phase and gas phase, the excess consumption on purge gas has to do with the temperature depression, which occurs during the desorption of the adsorbent in the last purged and still heavily loaded adsorbent layer. In the laboratory scale, that is with a large surface compared to mass and good heat transfer, this effect is hardly noticeable; in technical installations, however, it could be clearly observed. The arrangement of the storage masses at the end of the adsorbent layer causes that this effect does not work out to a disadvantage. As a consequence of the partial unloading principle, the retained load in the adsorbent along the retained load front prevents the adsorption heat during adsorption from concentrating in a small space, but distributes it over a greater distance, whereby the above mentioned climbing temperature curve towards the adsorbent end and a better thermic effectivenessare achieved. Vice versa in a fully desorbed adsorbent, a large amount of heat would become free in a small space, which considering the reversible operation would the especially disadvantageous, if as in the Sorbogen II Process (Picture 7) for special reasons the temperature gradient along the orbent layer is increased through heating respectively cooling

apparatus between exchangers and adsorbers to bind and eventually enrich the volatile impurities respectively gas components.

# Sorbogen II Process

Here, a cooling apparatus at the raw gas inlet, i.e., between the cold storage and the adsorbent, respectively, a heating apparatus at the clean gas outlet, i.e., between heat storage and the adsorbent, is arranged. This system allows to heat and cool both branches constantly, and at the same time. Thereby, time is gained for precooling, respectively preheating, of the storage masses which are precooling the raw gas, respectively preheating, the purge gas. The mutual influencing of heating and cooling apparatus is prevented through regular cycling and maintaining of a temperature curve along the adsorbent layer. Depending on the flow condition in the prevailing cycle, the cooling apparatus either cools the raw gas before its entry into the adsorbent or after cycling the outgoing loaded purge gas befor. it enters into the cold storage, which now after its temporary partial warming by the raw gas, is being blown cold again (Picture 7). During one period, the heating apparatus heats the purge gas which has been preheated by the heat storage before it goes into the adsorbent. During the following period, it (the heat apparatus) heats the purified gas before it goes into the purified gas before it goes into the adjoining precooled heat storage. The heat Storage can therefore, after cycling, preheat efficiently the purge gas. Of course, also in this arrangement the adsorbents and storage masses are kept in a constantly maintained temperature curve, whereby the free end of the storage is always near the ambient temperature (Picture 8). Here also, (again) the change of the temperature of a particle of raw respectively purge, gas flowing through the apparatus shortly before cycling is schematically shown. Under the influence of heating and cooling the temperature curves of raw and purge gas cross over. The dot-dash line again shows the course of the mean temperature of the adsorbent, respectively the storage mass. Advantageous in this arrangement/the reinforcing of the heating effect by the adsorption heat carried towards the adsorbent end and the reinforcing of the effect of the cooling apparatus by the desorption cold carried towards adsorbent start. Also this arrangement enables a nearly reversible operation down to the area of very low temperature with a corresponding steep temperature curve. As we already mentioned above, an excess of purge gas over raw gas is no longer needed at a temperature increase of 10°C.

If one wishes to recapture the adsorbed gas components a further increase of the temperature difference with concurrent reduction of the purge gas volume is adequate. An additional possibility of enrichment exists in the expedient desorption at sub (lower) pressure and, in the sense of the above execution, by maintaining a counterflow purge. In these circumstances, one can also use as purge gas, a partial flow of the clean gas branched off downstream from the adsorbent. The use of a moderately higher pressure, i.e., 2-10atm., during the adsorption of the adsorbent is advantageous in case the cleaned

gas shall be available under pressure. At higher pressures, the gas losses increase at cycling under certain circumstances beyond an acceptable figure as also part of the cleaned gas is adsorbed and is lost during the pressure reduction at cycling. The technical utilization of Sorbogen I Process, as well as the preparatory experiments for it, will be reported in a following later article.

## Summary

The process and apparatus prerequisites for an approximate reversible operation (called Sorbogen I Process) in the cleaning of gases through adsorption with relatively short duration cycling of the adsorber, preferably for the purpose of further fractionating of the cleaned gas under elevated pressure and at lowered temperature, are explained. Due to the similarity of the cycling operation as well as the thermal and matter exchange characteristics, the process is being compared with the process of gas purifying by means of cold generators.

On hand of schematics, drawings and diagrams, the principles of "reversible" operation, namely the heat exchange between adsorption (loading) and desorption (unloading) process, even without use of foreign heat and cooling sources, creexplained. A condition to achieve a maximum purifying effect even in the removal of difficult to adsorb impurities is the maintaining of a very large free (unloaded) zone. This is called the principle of "partial loading". A "reversible" operation is promoted through use of the principle of "partial loading". The known and always consistently applied purge degasing with clean purge gas in counterflow to the raw gas is a further prerequisite for the highest purity effect as well as for "reversible" operation. The work method for enrichment and gaining of the adsorbable components (called Sorbogen II Process), utilizing the same principles and with most economical use of energy for heating and cooling together with the prerequisites of the apparatus for it, are given.

## Submitted August 11, 1952 and

- 1) Dtsch. Patentanm. G 6724 IV b/12e.
- 2) Dtsch. Patentanm. P 22 720 IV b/12eD.
- 3) Dtsch. Patentanm. G 405 IV b/12e.
- 4) Dtsch. Patentanm. G 94 IV b/12e.

# DEFENDANTS' EXHIBIT S(5)

That portion of Pearlman Affidavit, filed September 25, 1967, designated Exhibit 11.

·, E-181

September 14, 1961

ピットンル

Heatless Dryer

### FILE MEMORANDUM

Mr. Whelen, Dr. Nagel and the writer visited the Kahn & Coplant at Wethersfield, Conn. on Saturday, Sept. 9, 1951 for the purper of reviewing the patent and licensing situation in the heatless dryer field with Kahn & Co. During the first part of the meeting Kahn & Co. was represented by Robert S. Sheldon, Vice President and Ervin B. Steinberg, Patent Attorney. Irving I. Kahn, President, joined us later when possible bases for settlement were being discussed. Kahn & Co. has an attractive modern plant on the cutskirts of Wethersfield, near Hartford.

Mr. Shelden started the discussion by explaining that the Kahn heatless dryer had been a natural outgrowth of Kahn's manufacture of heated dryers and other test equipment (mainly for military ground support) and simply represented a routine development based on sound engineering principles. He claimed that Kahn's heatless dryer was developed before the Kahn people heard anything of Skarstrom's or Trinity's work in the same field. Later on Mr. Kahn explained that his company has a very substantial engineering staff devoted to research and deviopment. (25 engineers out of a total force of about 85.)

Mr. Steinberg then told us that he has made a rather cursory search of the prior art in the Patent Office which has led to believe that our Skarstrom patent lacked invention.

He gave us a list of the references which he considers pertinent. These include the British (Linde) 677,150; the art cit against U.S. 2,955,673 (Kennedy et al); as well as some other pate such as U.S. 1,682,588; British 633,137; and German patents 882,54 972,223. We immediately replied that we, as well as Kenyon and Ke have been aware of most of the art on Mr. Steinberg's list, including the British Linde patent which in our view represented the best prior art not made of record against Skarstrom. For that reason we stated that offhand we felt that the art referred to by Mr. Steinberg has not materially changed anything, including Kenyon's Kenyon's opinion that many of the important process claims of the Skarstrom patent U.S. 2,944,627 were valid and applicable to the operation of the Kahn dryer we have in effect admitted that Skarstrom's apparatus claims don't apply to the Kahn dryer.

During the discussion Steinberg made the point that Kahn dryers usually operated with long cycles of 6 minutes or more, which were substantially longer than anything disclosed in Skarstrom's specification and therefore could not be validly covered by Skarstrom's claims. We replied that we saw no reason why a court or anyone classically read any limitation on cycle length into the claims on the upplication.

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of an infringer merely because the infringer operated at numerical values higher than the examplary numbers disclosed in the patent specification. We have assured the Kahn people that we had no intention of enforcing our patent if they can convince us of its invalidity, e.g. if they can cite us the existence of a commercially invalidity, e.g. if they can cite us the existence of a commercially used heatless dryer prior to Sharstrom's invention date. The Kahn used heatless dryer prior to Sharstrom's invention date. people have tentatively admitted that they did not know of any such instance but they might want to try checking into it further.

In response to Mr. Steinberg's request we stated that in our view the essence of the Skarstrom invention involved a combination of the following three features.

1. Reversal of the drying cycle prior to breakthrough;

2. Use of dry product gas for purge; and 3. Utilization of heat of adsorption for driving off moisture during description without use of extraneous heat.

The Kalmrepresentatives replied that reversal of the drying eyele before breakthrough was conventional in any kind of adsorbtive drying. (This is not entirely true since many references speak of regenerating the adsorbent after it has been "saturated".) The use of product gas for purgo has been shown in the prior art by Kahle and others, and employment of the heatless principle has been taught by the British Linde patent. We then retorted that while Mr. Steinberg's analysis of the individual references may be correct we nevertheless know of no prior art suggesting the combination claimed by Skarstrom or the unobvious result achieved thereby, and for that reason we had full faith in the Kenyon and Kenyon opinion concerning validity. However, we have agreed that we would carefully review those references on Mr. Steinberg's list which we had not seen previously and that we of course, reconsider our position if these references showed anything more portinent then the other prior art of which we had been aware. We have indicated that we did not consider this likely. Mr. Steinberg has requested that we supply Kahn and Co. with our reasons, as to the grounds on which Skarstrom's most pertinent claims (c.g. claims 9, 16 and 17) should be considered patentable over the art referred to by Mr. Steinberg.

Next Mr. Steinberg suggested that Kahn & Co. was of course interested in an amicable settlement and that they would be willing to make one even though they considered the Skarstrem patent of very . doubtful validity. Specifically he said that they would be willing to nettle on the basis of obtaining a paid-up license for Kehn & Co. under our Skarstrom patent in return for a paid-up license to "Esso" under Kahn's Kennedy et al patent. We emplained that such a license to "Esso" would be worthless to us since we were not in the dayer manufacturing business. Steinberg replied that he didn't have authority to go beyond the proposition he had just made but that this point seemed to present an opportune moment for having Mr. Kalm join us in our discussion. Mr. Kahn did join us at this point.

When we explained to him that a license under the Kennedy et al patent to Esse would be of no value to us he replied that he would of course include licensing rights to third parties along with a license to Esso. When pressed further by Mr. Whelan as to whether such licensing rights under the Kennedy patent would be exclusive, Mr. Kabo replied he would be willing to make such a grant exclusive subject only to retaining a license under the Kennedy et al patent for his own operations. Next Mr. Unelan expressed serious doubts that even the last proposition could be of any interest to us since it (would hardly be made compatible with the "most favored licensee" clause in our standard heatless dryer licenses. For this reason, Mr. Whelan suggested that while he did not have authority to make any specific proposals he would be prepared to ask our Management's approval for a settlement with Kahn on the basis of Kahn & Co. taking a standard heatless dryer license from us under Skarstrom and Esso getting an exclusive license and licensing right from Kahn under the Kennedy et al patent, with the net effect that Kahn would pay us the regular 10% royalty on 2-bed dryers, no royalty at all on 1-bed dryers, and we would pay over to Kahn up to perhaps as much as 50% of royalties hereafter received from our other licensees on their 1-vessel dryers covered by the Kennedy et al patent.

Mr. Kahn did not seem particularly interested in our counterproposal for two reasons. First, he felt our Skarstrem patent was of such doubtful validity that anything other than a paid-up license on more or less neminal terms would not be acceptable to him as a matter of principle. He expressed the thought that a large company such as Esso should not use a weak patent such as Skarstrem to impose burdensome royalties on "small business". To this we replied that we had an opinion from outside counsel assuring us that we had an enforceable patent, that this patent has received extensive recognition Mr. Kahn did not seem particularly interested in our that we had an opinion from outside counsel assuring us that we had an enforceable patent, that this patent has received extensive recognition of the industry and that we therefore were preceding with our licensing program not only in reliance on the best legal advice available to us but also in fair discharge of our contractual obligations to our existing licensees. Incidentally, Kahn also expressed displeasure at our notifying his customers such as General Electric of our Sharstrom patent and its possible applicability to their operations. We told him that this was the only way we could properly bring our patent rights to the attention of those concerned, especially since Kahn & Co. itself had shown little interest in pursuing the matter directly with us when we first contacted them. Kahn also was somewhat irritated by the fact that some of Trinity's salesmen had been cautioning prospective customers about our patent long before it had issued. We believe we customers about our patent long before it had issued. We believe we have satisfied Kahn that any such actions were undertaken entirely without our knowledge or consent.

Kahn's second objection to our counterproposal was that even though it conceivably could be more advantageous to him in the long run than his own original proposal if the one-bed dryer proved to be extensively used, he felt that it would leave his company's future royalty obligations in an undesirable state of uncertainty.

The meeting was conducted throughout on a friendly and f factual basis by representatives of both parties. Our impression of Kahn & Co. and especially of the apparent competence and alertness of its technical staff and management has been considerably better than what some of our present licensees have led us to expect. Mevertheless, the respective positions of the parties at the end of our meeting have remained very far apart. The prospects of finding a common meeting ground are not very bright. Consequently, we should proceed quickly with a further review of the art cited by Kahn, obtain Management approval for a definite offer to be submitted to Kahn and institute legal proceedings against Kalm promptly if Kahn does not accept our offer soon after we submit it to him.

PETER H. SMOLKA

### PEStros

ce: Mosses. W. C. Asbury
E. J. Eronnor
M. R. Mandelbaum
F. L. Miller
R. H. Nagel
P. J. Whelan

P.S. At lunch we discussed with the Kahn representatives miscellaneous general topies. Kahn emplained that his company got into the military test equipment business in the early post-war years and added the conventional heated dryers to their line of products around 1952-53. Their line of products now also includes a dew point analyzer. We informed them that we had some patents in this field also, and they have expressed a desire to see them. We plan to send them copies of our pertinent patents shortly. general topies. Kehn emplained that his company got into the

DEFENDANTS' EXHIBIT U(5)

Claim Analysis Chart

#### ANALYSIS OF THE CLAIMS OF THE PATENT IN SUIT

WHERE CI IN THE PATEN

#### PRINCIPAL PROCESS STEPS CLAIMED

Step 1	flowing primary air under high pressure through a first bed of adsorbent in one direction to remove moisture from the air

All Accuse Disclaimed

Step 2 flowing a portion of the dried air (from Step 1) under reduced pressure through the same or a second bed of adsorbent in a reverse direction to remove moisture from the adsorbent

All Accuse Disclaime

Step 3 reversing the cycle

All Accus Disclaime Except Cl

#### FLOW CONTROL LIMITATIONS CLAIMED

- A. With respect to the extent of adsorption and desorption
  - duration of flow in each direction is less than that required to reach saturation or moisture equilibrium of the air and adsorbent

All Accus Disclaime

AIMED IT IN SUIT	WHERE DESCRIBED IN THE PATENT IN SUIT	COMMENTS ON NOVELTY
ed and i Claims	Col. 6, lines 7-24 Col. 8, lines 37-52 Col. 17, lines 25-30	
ed and d Claims	Col. 6, lines 25-42 Col. 8, lines 53-75 Col. 17, lines 36-47	Disclaimed subject m Kahle German 871,886
ed and d Claims aim 9	Col. 3, lines 40-50 Col. 8, lines 12-13	

Col. 12, lines 28-31 Col. 17, lines 30-33

ed and d Claims Disclaimed subject matter disclosed in Dai 871,886\*; Kahle German 970,223\*; Chemi Ing Erdmann U.S. 2,254,799\*

OF THE PATENT IN SUIT	(	WHERE CLAIMED IN THE PATENT IN SUIT	WHERE DESCRIBED IN THE PATENT IN SUIT
IMED			
mary air under high pressure irst bed of adsorbent in one o remove moisture from the		All Accused and Disclaimed Claims	Col. 6, lines 7-24 Col. 8, lines 37-52 Col. 17, lines 25-30
ortion of the dried air (from er reduced pressure through a second bed of adsorbent in irection to remove moisture sorbent		All Accused and Disclaimed Claims	Col. 6, lines 25-42 Col. 8, lines 53-75 Col. 17, lines 36-47
le cycle	· • • • • • • • • • • • • • • • • • • •	All Accused and Disclaimed Claims Except Claim 9	Col. 3, lines 40-50 Col. 8, lines 12-13

All Accused and Disclaimed Claims

Col. 12, lines 28-31 Col. 17, lines 30-33

IMED

nt of adsorption and desorption

flow in each direction is less quired to reach saturation or ilibrium of the air and adsorb-

Disclaimed subject matter disclosed in Kahle German 871,886\*

Disclaimed subject matter disclosed in Dailey U.S. 2,535,902\*; Kahle German 871,886\*; Kahle German 970,223\*; Chemi Ingenieur Technik\* Br 633,137\*; Erdmann U.S. 2,254,799\*

2	<b>!.</b>	duration of flows in opposite directions will develop an oscillating concentration of misture within bed during both adsorpt on and desorption which oscillates within the limits of the bed	Accused Cla
	3.	duration of flows in opposite directions will cause the partial pressure of the moisture in the air after desorption to be about the same as that in the primary air before adsorption	Accused C1
	4.	volume of dried air (at high pressure) used for desorption bears same ratio to total volume of dried air as ratio of absolute pressure of the desorption unit to that of adsorption unit	Accused C1
	5.	duration of flows in each direction is suf- ficient to produce substantial equilibrium of moisture in the air and adsorbent at the entrance end of the bed during adsorp- tion and at the exit end of the bed during desorption	Accused C1
B. With	respe	ect to temperature	
		duration of flow in each direction is suf- ficiently short so that the heats of ad- sorption and desorption are substantially balanced and temperature of adsorbent bed remains substantially ambient	Accused C
ADDADATI	IS I.TM	TATION CLAIMED	

## APPARATUS LIMITATION CLAIMED

The adsorbent beds are self-contained with respect to the transfer of heat.

Accused C

im 9	Col. 12, lines 24-28 Col. 17, lines 52-56	Inherent result of Al (See col. 12, lines 24-28 of patent in suit)	Disclosed Kahle Ger
aims 12 & 14	Col. 7, lines 44-48	Inherent result of Process Step 2 (see col. 7, lines 44-48 of patent in suit); also an inherent result if amount of water adsorbed is to equal amount of water desorbed	Disclos U.S. 2
aim 24	Col. 9, lines 5-46	Inherent requirement if amount of water adsorbed is to equal amount of water desorbed (see col. 9, lines 19-24 of patent in suit)	Disclos German
aim 34	Col. 11, lines 43-47	Inherent result of Process Steps 1 and 2	Inhere Kahle
laims 9 & 16	Col. 6, lines 45-76 Col. 7, lines 1-16	Disclosed in MacMullin U.S. 2, Kahle German 970,223*	340,398*; K
laim 17	(meaning indefinite) possibly refers to Col. 6, lines 73-75 Col. 7, lines 1-8 Col. 7, lines 28-34	Operation without heaters and Chemi Ingenieur Technik*	coolers dis
		* Not considered by Patent Off	ice

flows in opposite directions of an oscillating concentration within bed during both adsorp- corption which oscillates with- cs of the bed	Accused Claim 9	Col. 12, lines 24-28 Col. 17, lines 52-56
f flows in opposite directions the partial pressure of the the air after desorption to he same as that in the primary adsorption	Accused Claims 12 & 14	Col. 7, lines 44-48
dried air (at high pressure) esorption bears same ratio to me of dried air as ratio of ressure of the desorption unit adsorption unit	Accused Claim 24	Col. 9, lines 5-46
f flows in each direction is suf- produce substantial equilibrium e in the air and adsorbent at ce end of the bed during adsorp- t the exit end of the bed during	Accused Claim 34	Col. 11, lines 43-47
ature  f flow in each direction is suf- short so that the heats of ad- nd desorption are substantially nd temperature of adsorbent bed bstantially ambient	Accused Claims 9 ६ 16	Col. 6, lines 45-76 Col. 7, lines 1-16
ED self-contained with respect to	Accused Claim 17	(meaning indefinite) possibly refers to Col. 6, lines 73-75 Col. 7, lines 1-8 Col. 7, lines 28-34

- -

Inherent result of Al (See col. 12, lines 24-28 of patent in suit) Disclosed in Dailey U.S. 2,535,902\*; Kahle German 871,886\* Chemi Ingenieur Technik\*

Inherent result of Process
Step 2 (see col. 7, lines
44-48 of patent in suit);
also an inherent result if
amount of water adsorbed is to
equal amount of water desorbed

Disclosed in Erdman U.S. 2,254,799\*

Balancing amount of water adsorbed and desorbed is disclosed in:

Inherent requirement if amount of water adsorbed is to equal amount of water desorbed (see col. 9, lines 19-24 of patent in suit)

Disclosed in Kahle German 970,223\* Kahle German 970,223\*; MacMullin U.S. 2,340,398\*

Inherent result of Process Steps 1 and 2 Inherent result in Kahle German 871,886\*

Disclosed in MacMullin U.S. 2,340,398\*; Kahle German 871,886\*; Kahle German 970,223\*

Operation without heaters and coolers discussed in Kahle German 871,886\*; Chemi Ingenieur Technik\*

<sup>\*</sup> Not considered by Patent Office

DEFENDANTS' EXHIBIT V(5)

Documents Produced with Plaintiff's Answers to Interrogatories

# DR. REF. N. T. J.-DETLEV FRHR. VC UEXKÜLL PATENTANWALT

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BANKKONTEN: DRESDNER BANK AG.
HAMBURG, KONTO-NR. 17019
HARVARD TRUST COMPANY,
CAMBRIDGE/MASS. USA
POSTSCHECKKONTO: HAMBURG 2558 72
TELEGRAMMADRESSE: UEXPAT
TELEFON: 82 67 02 UND 82 03 65

UVED.

FEB 14 1964

2 HAMBURG-HOCHKAMP.

February 11, 1964 ue:ro/2681

Re: German Patent Application E 60 071 based on U.S. Ser.Nos. 670,342 and 714, 780 - My File: 2681

Dear Mr. Veryard.

This is to summarize what we discussed with respect to the above mentioned patent application during your stay on February 5 and 6, 1964 in Hamburg.

1) I informed you that I am not at all hopeful with the further procedure of the present application, especially if one considers German patents 871 886 and 970 223 of LINDE, and the article in "Chemie Ing. Techn.", 1953 vol. 3 of Dr. Kahle who is inventor of both German patents. These citations not yet mentioned by the examiner will be probably cited by opposing parties, and especially by Linde.

We first discussed the general way of drafting German claims, and the necessity to define the invention - i.e. the new features - in the characterizing part of such claim. If one cannot distinguish the invention in writing a claim in such a way, then there will probably be no chance to get a patent. It is not sufficient to state that the invention is distinguished over patent A by features XYZ and is distinguished over patent B by the features UVW. I admit,

80. M.

however, that in some cases it is possible to use one citation as a basis for the prior art and only this citation can be used in the precharacterizing part of the claim whereby other features may be included into the characterizing part as being "known per se". This approach is very similar to the usual Dutch procedure. In Germany, however, this is only recommendable or possible if the citations are not that closely related to each other as it is the case with German patents 871 886 and 970 223, which besides all are already combined in the article of Dr. Kahle in "Chem.Ing.Techn."

2)You informed me about the many important advantages and stated that up to now nobody has tried to work according to the present invention. Although I appreciate this, one has to keep in mind that the level of invention (Erfindunghöhe) has nothing to do with the advantage of an invention (Fortschrittlichkeit). Even very high advantages cannot be used to compensate a low level of invention and vice versa.

Contrary to the attitude of the Dutch patent practice where one starts from one citation, one has generally to acknowledge all the prior art in the precharacterizing clause. If you are able to draft such a claim, then it is easier to defend the application also against the argument of insufficient level of invention. Namely, if the only feature is "known per se" then there would be no invention to combine the known features with other features being known from other citations in the same field. The so called "combination-inventions" are difficult to defend as long as they refer to method claims.

3) If one considers the two German patents 871 886 and 970 223 one has to admit that they have the following features or objects in common with the present invention:

- a) they all refer to a method for removal or recovery of components from streaming gas mixtures. It is irrelevant whether this is named "fractionating of gases" or whether this is defined in any other more or less complicated way by making reference to "one or more components" etc.
- b) they all refer to a periodical alternating selective adsorption and desorption whereby the current flow directions are opposite to each other. Such wording also implies that there must be an adsorbing material which selectively adsorbes one or more components.
- c) It is further known that the feed gas is fed at a higher pressure and that the desorption takes place at a lower pressure (please compare German patent 871 886, page 2 left column, line 27 - 45). This passage refers to the adsorption and desorption carried out at the same temperature, namely at adiabatic conditions - and it is stated that the volume of the stripping gas has to be equal to the volume of the feed gas and can be twice or three times as much (if the same pressure is used). Here it is further stated that the desorption can take place by using . a depressurized effluent from the adsorbing step having the same temperature and - further - by using . only a part of the primary effluent. It is further stated that a part of the primary effluent being not used as stripping gas for the adsorber can be obtained in pure state if the difference in pressure is sufficiently high. Therefore, the next common feature is:
- d) A part of the effluent gas from the adsorber is used as stripping gas in all cases.

4) A further analysis of the citations shows that it is known from German patent 871 886 to step or interrupt the desorption at a point when the loading of the stripping gas with the component to be desorbed decreases. Similarly, German patent 970 223 states that the adsorbing material is not completely loaded with the component to be adsorbed. We called this during our conference "shallow breathing". We believe that this is different from what happens in the present invention where the stripping gas is fed through the desorber until the desorber is practically free from humidity, and vice versa, the adsorber is fed with the humid air until the material is nearly completely loaded up to its capacity.

If this assumption is true, then we have the first characterizing feature, namely

x) that the adsorption is interrupted shortly refore the saturation, and the desorption is interrupted shortly before the complete exhaustion of the adsorption material.

Keeping in mind the pulsating front and the general idea of the present invention we thought that the duration of the cycles could give us a further feature for the characterizing part. We called this duration of the cycle also "switching period". A similar expression is used in German patents 871 886 and 970 223. Here it is stated in 871 886 on page 2, right column line 80 - 84 that after several cycles an additional desorption has to take place, e.g. after some hundred switchings which is necessary after a few days or weeks. This means that the switching period of patent 871 886 is more than one hour. On the other hand it is mentioned in German patent 970 223 that switching periods of 5 - 30 minutes can be used. This patent refers on page 2,

- 5 -

right column, line 110 to German patent 624 912 disclosing switching periods below half an hour; and further on page 3, line 10, to German patent 704 073 disclosing even shorter switching periods. This patent 704 073 refers on page 3, line 14 - 19 to switching periods which are in the dimension of minutes (copies of these two further patents have been ordered and will be forwarded to you in due time).

If the next characterizing feature should be the time, then this time should be better explained with respect to the equilibrium which is reached and also with respect to the forming of a pulsating front. The description of the present invention refers to an upper time limit of less than 2 - 3 minutes, a preferable upper limit of less than 1 minute, and a further preferred switching period of less than 10 seconds. It would be much better to use shorter time limits in the characterizing part; however, you informed me that said period is actually about two minutes. For the better explanation of this period I recommended a more functional feature which will be very helpful if the examiner agrees. This feature would be

y1) that the desorption period and adsorption period, respectively, are in each case less than 2 - 3 minutes so that no equilibrium is reached in the adsorption bed and desorption bed, respectively, between the bed and the component to be adsorbed and desorbed, respectively.

This feature y) can be further explained by another even more functional phrase, namely in that:

y2) a pulsating front is formed between inlet opening and outlet opening which corresponds to the equilibrium between the vapour pressure of the component to be separated in the gas and the vapour pressure of this component on the adsorption material.

To complicate the claim and to confuse others - but not for the better definition of the invention - one can add a further feature, namely

that the amount R of the stripping gas corresponds to the equation  $R = \frac{(R+D)}{P_1 / P_2}$  in which the value (R+D) corresponds to the amount of the effluent gas from the adsorber.

As mentioned above, this feature z) is not a real feature characterizing the present invention because no absolute values are disclosed for P1 and P2. The description mentions a ratio of 4:1 and also a ratio of 6:1. These, however, are not considered to be essential or critical. That this equation is moreor less meaningless without giving any absolute values follows when one assumes that P1 and P2 are nearly equal; in such case all the effluent or primary product has to be used as stripping gas. This, however, is already mentioned in German patent 871 886 on page 2, left column. Here it is stated that there are several possibilities when working according to the method of patent 871 886. Temperature, pressure and volume are related to each other. If the temperature is not changed, then the volume of the stripping gas has to be increased; if a pressure difference is created, then one does not need a larger volume, but can use only a part of the volume. The other possibility (passage b) on line 46 - 52 discloses a difference in temperature which gives the possibility to reduce the stripping gas volume to 1/30 to 1/20 of the feed gas volume. If the volumes during adsorption and desorption are similar or equal, then a temperature difference of about 5° C can be used when working near room temperature.

- 5) Based on the analysis as mentioned above we agreed on a claim 1 for the method as per enclosed copy. The English version of this claim is also enclosed. The language is completely different from what is used in the States, but the systems and philosophy are different, too. Finally, it is completely irrelevant whether one uses the phrase "adiabatic" or "substantially adiabatic"; whether one refers to the adsorption of one component or of one or more components; it is not necessary to mention that a raw gas is fed to the bed and that a pure product is obtained. All this is implied in the general meaning of the precharacterizing part. You will note that the German patents 871 886 and 970 225 have a similar abrupt and, according to your feeling, an insufficient wording.
- 6) During discussion of the present invention we discovered some inconsistencies, or at least, passages which I believe are inconsistent, such as
  - A) if the amount of the stripping gas and of the effluent gas is given in dimensions of litres per minute, at standard conditions, one has a rather indefinite dimension. I assume that the equation is also valid if the dimensions are grams or moles. Please enlighten me on this.
  - B) It would be good if you could confirm that the present invention has nothing to do what we called "shallow breathing", and further, that our definition of the feature y1) and y2) is correct.
- 7) Our general attitude with respect to this case was that it is better to have this application published with a rather restricted claim than getting away with a broader claim and having difficulties with opposers later on.

  This may be the case if the examiner is not aware of German patents 871 886 and 970 223; if they are cited

later during an opposition procedure - and there is no reason to believe that Linde will not file an opposition then it is much more difficult to convince the Patent Office that these citations have nothing to do with the present invention. It is not necessary to mention the numbers of these German patents for the examiner, but one has to draft the description in such a way that one can later on state that these patents have already been acknowledged in the description. Once you have obtained a patent on the narrowest claim you can ever think of, there will be less difficulties in broadening the ghist of this invention during an infringement procedure, than in defending the published application having a broader claim during opposition because the invention is - as I believe - pretty close to what is disclosed in German patents 871 886 and 970 223.

The drafting of the further subclaims and claims being directed to an apparatus should be postponed until you agree with the general procedure as outlined above. You know that it takes some time to draft good claims, but I assume that I can send you the proposals within a week or so after having received your agreement with this claim 1. I would further recommend to file the new claims together with a rewritten description.

g) For the time being there is no term pending, however, the examiner requested with letter of November 7, 1963 that it has to be stated what priorities cover the respective claims. This was not yet mentioned; only the certified copies have been filed. Because of the other patent application of a third party the priority of which being within between the two priorities you are claiming for the present invention it may be possible that the examination of the present case is suspended. This,

however, should be avoided because you are probably not interested in keeping this application unpublished for more than several years.

Please let me have your instructions in due time.

Very truly yours,

Enc.
proposed claim 1
in English and German

ec: EREC ESSO AG

## E-196 Proposed Claim 1

Method for adiabatic removal or recovery of components from streaming gas mixtures by periodical alternating selective adsorption and desorption in current flow directions being, opposite to each other, the adsorption of one or more components of the feed gas at the higher pressure P1 is followed by a desorption at a lower pressure P2 using a part of the effluent gas from the adsorber as stripping gas, characterized in that the adsorption is interrupted shortly before the saturation, and the desorption is interrupted shortly before the complete exhaustion of the adsorption material and that the desorption period and adsorption periods, respectively, are in each case less than 2 - 3 minutes, so that no equilibrium is reached in the adsorption bed and desorption bed, respectively, between the bed and the component to be adsorbed and desorbed, respectively, but a pulsating front corresponding to the equilibrium between the vapour pressure of the component to be separated in the gas and on the adsorption material, and further that the amount R of the stripping gas corresponds to the equation  $R = \frac{(R + D)}{P_1 / P_2}$  in which the value (R+D) corresponds to the amount of the effluent gas from the adsorber.

# Vorschlag für Anspruch 1

Verfahren zur adiabatischen Entfernung 'oder Gewinnung von Komponenten aus strömenden Gasgemischen durch periodisch aufeinanderfolgende, selektive Adsorption und Desorption in entgegensetzter Strömungsrichtung, wobei sich an die bei erhöhtem Druck P, des Rohgases erfolgende Adsorption von ein oder mehr Komponenten eine bei niedrigerem Druck Po erfolgende Desorption mit einem Teil des aus dem Adsorber austretenden Gases als Spülgas anschließt, dadurch gekennzeichnet, daß die Adsorption kurz vor Sättigung des Adsorptionsmittels und die Desorption kurz vor vollständiger Erschöpfung des Adsorptionsmittels abgebrochen wird und die Adsorptions- und Desorptionsperiode jeweils weniger als 2 - 3 Minuten beträgt, so daß sich kein Gleichgewicht im Adsorptions- bzw. Desorptionsbett zwischen dem Bett und der zu adsorbierenden bzw. desorbierenden Komponente einstellt, sondern sich eine pulsierende, dem Gleichgewicht zwischen dem Dampfdruck der abzutrennenden Komponenten im Gas und auf dem Adsorptionsmittel entsprechende Front zwischen Eintrittsund Austrittsöffnung ausbildet, und daß ferner die Menge R des Spülgases der Gleichung  $R = \frac{(R + D)}{P_1/P_2}$  entspricht, in welcher der Wert (R+D) der Menge des aus dem Adsorber austretenden Gases entspricht.

E-198

# - DR. RER. AT. J.-DETLEV FRHR. VON EXKÜLL

11:17

BANKKONTEN: DRESDNER BANK AG, HAMBURG, KONTO-NR. 17019 HARVARD TRUST COMPANY, CAMBRIDGE/MAGS. USA POSTSCHECKKONTO: HAMBURG 2558 72 TELEGRAMMADRESSE: UEXPAT TELEPHON: 826702 UND ÜBER 620365

International Patent Causes
P.O. Box 243

Elizabeth, M.J. / USA

HAMBURG-HOCHKAMP,

MAGEVED

MAY 13 1954

May 11, 1964 2681 / St:mü

Re: German Patent Appln. E 16 071 Based on US 670,342

My File 2681

Dear Dr. Marx:

Further to my letter of April 22, 1964 please find enclosed a set of new claims and a translation thereof.

After having again carefully studied the citations in the light of Mr. Ceccon's letter of February 28, 1964 I would recommend to file the enclosed new claims.

The precharacterizing clause of the new main claim was drafted to cover practically all features, which the present invention has in common with the methods disclosed in the German patents 871,886 and 970,223. In the characterizing part I used the wording: "...at least two adsorption beds of which at least one is on adsorption and at least one is on desorption ..." because the above German patents, while referring to the use of two or more beds, do not mention that one bed should be on adsorption during desorption of the other. If the Examiner raises the objection that the latter feature is known per se from other prior art, we could either add the phrase "known per se" to this feature or, if necessary, transfer it to the precharacterizing clause.

As already mentioned in my letter of February 11, 1964, I have serious doubts whether we will succeed to obtain protection for the present case, because the German patents 871,886 and 970,223 are really close prior art.

•

There are a few features in the present application, which could be used with some hope, to defend the invention. Firstly the present invention comprises the proposal to use as purge stream a part of the product gas stream corresponding to not more than the absolute ratio desorption pressure: product gas pressure.

Secondly the cycle time is restricted to less than 3 minutes.

Thirdly the apparatus described in the new claims 8 to 13 seems to be new and technically advantageous.

Accordingly in a new main claim it is important to make the above arguments the main features of the characterizing part.

Although the process according to the enclosed new main claim is apparently new and it will probably be also possible to substantiate a technical progress over the methods in the citations, the key question will be, whether we succeed to convince the Examiner (and the Federal Patent Tribunal in case of an opposition) of the level of invention. The decisive point will probably be, whether an expert knowing the prior art, especially the German patents 871 866 and 970 223, was able to arrive at the method of the invention without own inventive thoughts on the basis of his usual skill and knowledge.

Even if the process claims should be considered not admissible, there might be a better chance for maintaining the apparatus claims. I do not know, however, to which extent the features of the apparatus claims may already be known from other citations.

With respect to the process claims I wonder whether it would be acceptable to restrict the claims by stating that the loaded bed has to be depressurized in a direction opposite to the flow direction of the feed gas. This could serve as a further new and distinguishing feature. Adequate disclosure could probably be derived from the original description, especially the drawings. In my opinion depressurizing in a direction opposite to the flow direction of the feed gas should lead to several technical advantages, in that:

- a) the partial pressure gradient of the key components is moved already during depressurizing towards the feed gas inlet,
- b) probably the necessary purge gas volume is smaller and
- c) the section of the cod next to the purge gas inlet is not contaminated with the key components.

It should be possible therefore to make the feature of depressurizing in a direction opposite to the feed gas

flow a basis for a technical showing.

Although the above restriction would result in a less broad claim, it would probably strengthen our general position. In view of the dangerous prior art we probably will have to be happy if we succeed to obtain valid protection on a narrow claim (which in case of infringement will be interpreted by the judge to cover also the indirect subject of the invention).

In order to draft an effective response please let me know

- a) whether the new claims meet with your approval,
- b) which arguments could be brought forward to prove that the overage expert, based on the citations, was not able to arrive at the invention without own inventive thoughts,
- c) whether the restriction discussed above (or any other) appears acceptable,
- d) which features of the apparatus claims are considered new and inventive.

I shall revert to this case as soon as the answer of the Examiner to my letter of April 22, 1964 is received.

Very truly yours,

Page. (under sep. over) New Patent Claims and translation thereof

cc: K.J. Veryard, Esq. Dr.C. Medrow

bus

Moders, Maemocko & Muhl District 95 Duri dista 832 Communy

Gentlemen:

This is in reply to your letter of 5/11/64 and to the enclosed set of chains for which we thank you.

We have studied the proposed claims and found them quite satisfactory, especially in its different presentation of the cycles. We have only two comments to offer: (a) Claim 1, as translated, gives the impression that the part of product known as a purge stream through bed (2) during the first phase, is flown therethrough during the entire phase, rather than during "at least a portion of the phase (cycle). Can you reword the claim so as to incorporate this concept?; (b) the term "Key components" may, if you so desire, be more clearly defined as "selectively adsorbable components". However, this is a question of linguisties.

furning now to your latter, we agree that counter-feed depressurization is a limitation. However, it does not seem to us that it is too novel an idea. We feel that the claims on file already have this limitation; but we are all in fever of including it in the claim. Please note that claim I on file already read "flowing a gas mixture (feed)... interrupting the flow... reducing the pressure... desorbing... discharging said desorbed component from said bed in a flow direction opposite to that of said gas mixture...". As you see, the discharge is due not only to the effect of the product purge but to the inherent opening of the bed and lowering of the

pressure therein. Thus, your arguments are well taken. We wonder however, how you can fit this feature in claim I without being compelled to switch from the "phase" presentation of your claim draft to the "cycle" presentation of the claims on file.

Referring now to your questions:

- 1. The new claims meet substantially with our approval, small amendments hereto being presented hereabove.
- 2. We feel that no new arguments may be presented against the citations of record. We feel that you already have all the material on hand and we cannot but refer you to the enclosed copy of portions of a Brief sent to the Dutch Agent in which we discussed German Pat. 871,886 and 970,223 (Corresponding to British 677,150) at great lengths.
- 3. The restriction discussed above appears acceptable.
- 4. The features of the apparatus which are to be considered inventive are those which allow the process to be carried out that is, those which are responsible for the bed's purging by means of the product stremm. However, since each individual component of the apparatus (beds, valves, pipes, check valves, etc.) is known to the artisan, it becomes rather clearly deducible that it is the entire assembly which is nevel. Its compactness, ease of manufacturing, accessibility for repairs, applicability to any physical and structural set-up rendered the apparatus a success and is now being used in a multitude of plants. This is to be stressed. Just recently, we presented an affidavit to the Dutch Patent Office showing the tremendous success of the invention; in this affidavit we have shown that in the last five years, sales of the application amounted to over \$3,200,000, with royalties to the assignce of over \$290,000.

If you need additional information, please let us know. We trust that you will be in a position to prepare a suitable roply. --

Very truly yours.

C. Ceccon

CC:cjc cc: Dr. J. T. Tyson Dr. Medrow attachments June 11, 1965

Re: Germany E 16071
Based on U.S. 670,342
714,780

## VIA ALRMAIL

Dr. Detlev Von Uckkull Koniggratzstrasse 8 2 Hamburg-Hochkamp Cermany

Dear Sir:

Thank you for your letters of April 14 and May 14, 1965 and for your enalysis of the Examiner's allegations and objections made in the Official Action of April 1, 1965.

We have the feeling that the three parties concerned with this application, that is, the Examiner, the Agent and the Applicant are slowly (and to nobody's fault) sliding into diversionary discussions and argumentations of smaller and smaller order of magnitude, so that they are, so to speak, "losing sight of the forest, because of the trees".

- first of all remember, namely:
- (a) We are facing very close prior art. This has been recognized since 1952 as consisting of German Patent 871,886, German Patent 970,223 and an article by Kahle published in Chemie-Ing-Techn. on January 25, 1953. These are the three most pertinent references.
- (b) Practically each individual step of Applicant's process, when examined on a "broad" basis, may be found disclosed in one or another of these three references. But the combination of steps even broadly, is not available from the prior art.
- (c) The issue of "obviousness", easily concluded by the Examiner, does not exist, because Kahle, who is an authority in the field, did not succeed in his invention and did not visualize the possibility of the process which

-2-

Applicant is now claiming.

M. .

- (d) Applicant has proven to have obtained considerable commercial success, as it is visible from royalty revenues and from serious attempts to infringe our process.
- (c) Applicant has met with very strong opposition both in the U.S. and in the Dutch Patent Offices and it was only through a slow and difficult prosecution that the attitude of the Examining Bodies was changed and the patentability of our invention was asserted.
- B. Let us, now, compare in tabular form the seven broad aspects of our invention with the disclosures of the three above-mentioned closest references.

	Invention's features	German 871,888	German 970,223	Kahle's 1953 article	
1.	Adsorption is short of bed saturation &	Yes, as to saturation	Yes	Yes	
	preferably short of break through	questionable as to break through	e, -		
2.	Adsorption is at elevated pressure and desorption at lower pressure	Yes	Yes	Yes	
3.	Description is short of complete removal of adsorbed component	Yes	Yes	Yes	
4.	The process is cyclic,	/Yes	Yes	Yes	
5.	Part of the unadsorb- ed offluent gas is used to desorb	Ambiguous	No	Yes (but in heated Sorbogen process, 148)	II
6.	The heats of adsorption are balanced in the bed (conserved), thus elimating the need for external transfer of	mi-	Yes, l	out NO Lonable	
7.	There are no heaters in the bed or on gas	"Yos	?	Yes	

June 11, 1965 -3-

The above comparative analysis should be accepted as being correct. It agrees with studies made by U.S. attorneys, outside Counsel, technical authorities, U.S. Examiners, Dutch Examiners and British authorities.

- From this tabulation, we should attempt to reach a definite decision as to what claim can best protect us. Let us proceed by way of climination:
- I. A combination type method claim (e.g. claim 9 of U.S. Pat. 2,944,627) is not possible in Germany. Arguing that feature 6, possibly disclosed in Patent 970,223, cannot be found in Patent 871,886, while feature 5, embiguously dis-closed in Patent 871,886, is not taught by Patent 970,223 cannot be done when the citations are so closely related to one another.
- II. A combination-type method claim which contains in the preamble all the known features of a given citation and is characterized in brand terms by the feature or features undisclosed by the same citation is not admissible. This is a Dutch practice, which cannot be used in Germany, where one has to admostledge all the prior art. This, of necessity, practically eliminates broad characterizing aspects of the invention.
- III. A standard and acceptable method claim which is characterized by one or more broad features undisclosed by all the prior art acknowledged in the preamble may not be possible, because there is no broad characterizing feature clearly available to us. If one inspects the comparative tabulation given above, one finds only two features (No. 5 &6) which are "not taught" by two citations and "only questionably or ambiguously taught" by the third reference. These features claiming the conservation of heat without external transfer and the use of product gas however, are weak and it is doubtful if they will withstend and overcome the passage on page 4, lines 54-59 of Patent 970,223 (..."practically the whole of the heat of the adsorption process remains in the adsorber and is consequently usefully employed for the subsequent desorption".) However, see sub D.

IV. A standard and acceptable method claim similar to that sub III above but restricted in its characterization, appears to be your present goal. This is becoming less and less desirable, however. The first restriction resides in a desorption and adsorption pluss limited to a time period of desorption and adsorption pluss limited to a time period of less than 3 minutes. By this limitation, we set an upper limit of 5 minutes (total cycle = 6 minutes) and we distinguish over patent 970,223 which teaches a lower limit of 5 minutes (total cycle = 10 minutes). Nowever, your argument that "the range of protection of the claims in case of infringement is interpreted extensively " is not clearly understood. Where is the boundary line between our upper limit and Kahle's lower limit? In other words, when do you fall into the sphere of influence of the Kahle's patent? Our "infringers" would operate most probably with total cycle periods of 10 minutes. Is this not beyond our range of "extensive interpretation" and within Kahle's range of equally "extensive interpretation"? Consequently, we believe of equally "extensive interpretation"? Consequently, we believe that we should strive toward a broader characterization clause, because claims which are cyclically restrictive will apparently not be sufficiently protective.

The second restriction resides in the use of a quantity of backwashing product gas progressively decreasing to a value corresponding to not more than the ratio of absolute description pressure to absolute product gas pressure. This limitation is not objectionable on our part, because the rate of "progressive decrease" is not specified and may be any value. However, if the claim were to be characterized solely by this feature, we believe it to be insufficiently defendable against the Exeminer's arguments.

D. The above listing of possible claim language leaves us with only two alternatives. (At least we believe it to be so.)

The first elternative resides in the arguing strenuously that our process distinguishes over both German patents 871,886 and 970,223 (we are not mentioning Kahle's 1953 article) in that:

(a) neither citation discloses elembly the use of a part of the unadscribed effluent for description (Feature No. 5) and (b) neither citation discloses elembly the adiabatic conservation of heat without using external transfer means (feature No. 6). These two differentiating features are arrived at by interpreting (and convincing the examiner to interpret) the words "ambiguous" and "questionable" as definite negatives. The claim then could read somewhat as follows (compare with your proposed claim):

MAIN METHOD CLAIM: "A method of separating one or more components from a gaseous mixture by selective adsorption and subsequent description in which one or more adsorption bads alternatingly, are loaded in the adsorption phase by introducing the feed gas, and withdrawing the unadsorbed product gas, and are described in one description phase at a lower pressure by introducing a purge gas in the opposite direction, characterized in that in the description phase a loaded bed is depressurized to the description pressure and is backwashed with at least a part of the withdrawn product gas, and in that the heat of adsorption is cyclically conserved without employment of external heat transfer means.

The actual wording of this claim has been maintained, as much as possible, similar to that of your proposed claim. The Examiner's objections given in the first five lines of the first paragraph of the action have been overcome by inserting the objected features (direction of flow, withdrawal of unadsorbate) in the preamble of the claim. As to the alleged "broadening" of the claim, it should be argued that upper limits of cyclic operations have been described only illustratively with respect to certain specific feeds (air, etc.) and that the length of the cycle is a dependent variable based on the physical characteristics of the type thermo-conductivity and volumetric throughput of the feed, —the content of the adsorbable component in the feed, the pressure employed in the adsorption operation, and on the varying heats of adsorption generated. In other words, it should be argued that the rapidity of cyclic switching should be so controlled (as to time) that the accumulation of heat of adsorption on the adsorbing particles during the adsorption phase of the process is maintained at such low A T values that the heat accumulated during adsorption is readily available in situ during the-corption, in order to have the desired adiabatic conditions of operation. It should be, furthermore, argued that the two features characterizing the process (backwashing with unadsorbed product and conservation of heat without external means), and not disclosed in any reference, inclusive of the Swiss patent 212,189.

The second alternative resides in following the present Dutch prosecution system of claiming the apparatus. This, of course, is useful if there is sufficient inherency of process coverage in the apparatus claim and adequacy of the apparatus claim regarding the scope of coverage. The claim should be fairly broad and surong assurance should be had that, in case of litigation, our patent interests and rights are fully protected. The claim, then, would read somewhat as follows:

MAIN APPARATUS CLAIM: "An adsorption device having at least one adsorber adapted for periodically alternating operation and each adsorber having a bed of adsorbent solids, a crude gas supply line connected to each adsorber and connected, through a valve, to a main supply line, and a product gas discharge line connected to each adsorber, as well as scavenging gas supply and discharge conduits connected to each adsorber, the scavenging gas supply conduit being connected to the product gas discharge line and characterized in that the scavenging gas supply conduit (21) is connected through pressure reducing means (21a) to the product gas discharge line (12) and the product gas discharge line (12) and the product gas discharge line (12) on one hand and the scavenging gas supply conduit (21) and discharge conduit (17) on the other hand are so connected to each adsorber that, in operation, the adsorption and description in each adsorber are effected in opposite directions of flow through the bed, said adsorption device being adapted to operate without the provision of external heat transfer means."

Concluding, our present thinking on the subject is reflected by the following proposal:

- 1. To use as claim 1 the hereabove proposed main method claim.
- 2. To use as claim 2 your proposed method claim 2, characterized in that the backwashing gas is withdrawn from another bed.

- 3. To use as claim 3 your proposed method claim 7, dealing with the separation of water vapor and CO2 from air. The dependency should be on claims 1 and 2.
- 4. To use as claim 4 your proposed method claim 8, dealing with the separation of water vapor from air. The dependency should be on claims 1 and 2.
- 5. To use as claim 5 your proposed method claim 9, but dealing with the separation of oxygen from air. The shift from nitrogen to oxygen separation was effected in order to maintain uniform the direction of the effluent. The dependency should be on claims 1 & 2.
- 6. To use as claim 5, your proposed claim 10 dealing with the separation of nitrogen from air. The dependency should be on claims 1 and 2. The shift from oxygen to nitrogen was again effected in order to maintain uniform the direction of the effluent. Furthermore, amend the words "without backwashing" to read "with negligible backwashing", otherwise the claim is contradictory with the characterization of the main claim in which we state the use of a portion of the main effluent for description.
- 7. To use as claim 7 cur hereabove proposed apparatus clait. We believe that this might corstitute a strong second line of defense and a possible retrenchment in the event we cannot obtain the main method claim.
  - 8. To use as claim 8 the following claim:

"An adsorption device according to claim 7 and having two equal adsorbers each with a solid bed of adsorbent material and a crude gas supply line connected with each adsorber, with a plural valve connected to a main supply line, and a product gas discharge line connected with each adsorber and connected to the main product gas discharge line by means of a valve, and further comprising a scavenging gas connecting tube between the two crude gas supply lines, characterized in that the crude gas supply lines (5, 6) each have a non-return valve (9a, 9b) upstream of a three-way valve (13, 14), the latter being connected to the scavenging gas discharge line (17), and that there is also a scavenging gas connecting tube (22) at the scavenging side between the two discharge lines (7, 8) upstream of the non-return valves (7a, 8a), disposed in the discharge lines, which tube (22) is centrally fed via a throttle valve

(21a) from the pure gas discharge line (10) and also has a non-return valve (22a, 22b) on both sides of the supply line (21)."

9. To use as claim 9 the following claim:

"Adsorption device according to glaim 8 characterized in that, for the purpose of automatic operation the three-way valves (13, 14) are provided with a solenoidal servomechanism (19, 20)."

- 10. To use as claim 10 your proposed claim 11, properly depended. Please check however, the wording of the English translation, because it appears to be incomplete ("...into a product gas with increased, (what?)...").
- 11. Your proposed claims 2, 7, 8, 9, 10 and 11 are to be found in the attachment to your letter of May 14, 1965. They might eventually be deleted, at a future date, if strongly opposed by the Examiner (on the ground that they belong to the specification) and if sufficiently and adequately covered by the main method claim.

As you can gather from the particular language used in our proposed claims 7, 8 and 9, these are the apparatus claims being prosecuted in Holland and translated directly from the Dutch.

Turning now, to the passages of the office action not yet commented upon, we believe that the claims, as proposed, do not contain functional statements which might be objectionable and they are described for the most part in U.S. application 670,342, thus claiming the priority of July 5, 1957 (except for our proposed claims 6, 9 and 10, for which the priority of February 12, 1958 should be claimed).

We would like to hear from you, prior to filing a response to the outstanding official letter, especially on our proposed main method claim (claim 1) and on our reasoning on the topic of claim formulation. We will comment upon the remainder of your arguments given in your letters of April 14 and May 14 at a later date, i.e. after your reply to the present letter.

Also useful, will be to request it an interview with the German Examiner. It is our impression that this was once proposed but never carried out. If you need any personal assistance E-211 -9-June 11, 1965

Dr. Von Uoxkull

at the Mearing, please contact Mr. Veryard in London, who we feel confident will lend you all the necessary attention.

Very truly yours,

C. Ceccon

CC:cjg

cc: Regular Mail

Regular Mail
Dr. C. Medrow
Dr. J. T. Tyson Your comments on our proposed claims are invited. Please provide also to contact Dr.
Von Ueximili on possible personal assistance at the interview. The above proposed claims have been carefully studied also by the inventor Dr. Skarstrom.

## DR. RER. NAT. J.-DETLEV FRHR. VON UEXKÜLL

PATENTANWALT

International Patent Causes P.O. Box 243 Elizabeth, N.J. / USA

Attention: Mr. C Ceccon

RECEIVED

JUL 12 1965

BANKKONTEN : DRESDNER BANK AG, HAMBURG, KONTO-NR. 17019 HARVARD TRUST COMPANY, CAMBRIDGE/MASS. USA POSTSCHECKKONTO : HAMBURG 2558 72 TELEGRAMMADRESSE : UEXPAT TELEPHON : 82 67 02 UND ÜBER 82 03 65

HAMBURG-HOCHKAMP

July 8, 1965 2681 - St:en

German Patent Application No. E 16,071 based on U.S. 670,342 and 714,780 My File: 2681

Dear Mr. Ceccon:

Thank you for your letter of June 11, 1965 and your · detailed analysis of the case. My comments are set out below for your consideration in the order used in your letter.

I agree that (a) the German patents 871,886 and 970,223 are the most pertinent references and (b) practically each feature of the invention is known per se from one or both of these references. Although none of them discloses all features of the invention, they both dis-close combinations of most of its features. Since according to German practice the level of invention is destroyed, if the average expert knowing the prior art at the filing date of the present application was able to arrive at the invention without own inventive thoughts, it does not matter whether (c) Kahle at the filing date of his application visualized applicant's process. Likewise (d), commercial success does not prove that the invention meets the legal requirements for patentability, especially the necessary level of invention. Since apparently

(e) the corresponding U.S. patent was granted;

I would appreciate to receive a copy of the

issued patent specification.

as 670742. Example for lesser

to distinguish mer lessed inplose.

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I agree to the tabulated comparison of the features of the invention and the Mahle references with two exceptions. Firstly, in my opinion there is no doubt that German patent 970,223 discloses the method of eyelical neat conservation. Moreover, both German patents 67:,666 and 970,223 as well as the Mahle article (1953) clearly disclose that adsorption and description are effected at the same temperature. Secondly, cyclical heat conservation is a result rather than a teaching of the operating conditions. For both reasons the cyclical heat conservation itself will hardly provide a distinguishing feature.

yes har no dear

I agree to your conclusion that the claim versions I - III are not feasible although the Dutch C) practice to acknowledge in the precharacterizing clause only the reatures known from the most pertinent citation is not completely ruled out in Germany, if the invention is a combination. There is no question that a method claim with a restricted characterizing part (as discussed under IV) is less desirable than a broad method claim, however, in the present case we will have to strive for valid rather than broad protection. In this type of cases in which the level of invention is doubtful, the attempt to defend the broadest possible claim may jeopardize the chances to obtain protection for a restricted claim because the examiner after rejecting e broad claim due to lack of invention will tend to reject also a restricted version which probably would have been granted, if filed originally.

The objections to the level of invention could be best overcome by restricting the main claim with respect to the phase length and the purge gas volume. An upper limit for the phase length of less than 3 minutes can be based on adequate disclosure in the original documents and would distinguish the invention over the Kahle patents. As already mentioned according to German practice the claims in case of infringement are interpreted extensively. One cannot define, however, a "boundary" between infringing and non-infringing cycle times, because the Court will consider all circumstances of the case. The decisive question will be, whether the potential infringer makes use of the invention or merely operates under conditions known from the prior art. Thus, in the present case even a cycle time of 20 minutes would probably be considered infringing if the infringer uses the principle of the invention, namely a product gas purge and the adiabatic heat conservation.

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D) In order to obtain maximum protection we should maintain a set of method claims and a number of claims directed to an apparatus for carrying out the process covered by the method claims. While I agree that the use of product gas for purging the loaded bed is the main distinguishing feature, I see practically no chance to directly use the adiabatic heat conservation, which is known from German patent 970,223 in the main claim.

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With respect to the main method claim proposed in your letter I invite your attention to the following three points:

- 1) It will be necessary to acknowledge in the precharacterizing clause that it is known to carry out adsorption and desorption at substantially the same temperature.
  - 2) By insertion of the words "at least" the formulation "... backwashed with a part of the withdrawn product gas ..." is extended to cover also a purge with excess product gas (from other beds or earlier operation) and thus removes the intended upper limit for the purge gas volume, which is desirable to distinguish the invention over the Mahle patents. Since the process of the invention is technically useful only, if at least part of the product gas is recovered, the main claim should preferably exclude the the case, that the total product gas is permanently consumed as purge gas. This does not prevent a subclaim according to which during the start-up period the loaded bed is backwashed with the total product gas. Since the process of the invention will be inoperable, if too small a fraction of the product gas is used for description, the definition of the purge gas volume should preferably also contain a lower limit. Unfortunately, the only suitable basis is disclosed only in US-application 714,780. I would strongly recommend, however, to use a corresponding lower limit for the purge gas volume in one of the method subclaims.

المستغمر بلين بالمهديد

The passage proposed for the cyclical heat conservation gives no clear technical teaching and will definitely be considered functional. Since the desired adiabatic operation as well as the necessary limitation to both incomplete loading and desorption are actually the result of adequate phase length control, the latter is the appropriate

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feature to be referred to in the main claim, even if a definite upper limit for the phase length shall be avoided. In my opinion the clude adiabatic heat conservation is the state ment that the phase length is adjusted sufficiently short for both adiabatic heat conservation and creation of a loading front oscillating in an interest of the state clude adiabatic heat conservation is the statevation and creation of a loading front oscillating in an internal section of each bed.

In the main appairatus claim proposed in your letter the last 9 lines of the characterizing part will also be considered functional. I would suggest to file a main apparatus claim directed to an apparatus for carrying out the process according to the method claim, characterized in that the purge gas supply Iline is a branch of the product gas line led back via a pressure reducing means.

The proposed apparatus claim Greferring to the apparatus shown in fig. 1 appears unduly restricted and in this form will probably be rejected by the examiner as a mere repetition of an example. I would therefore suggest to file a somewhat broadened version. The "negligible backwashing" in your proposed claim 6 is not backed by the original disclosure. Moreover, such an amendment is unnecessary because according to German practice a subclaim may be a modified version of the invention defined in . the main claim.

In order to provide a second line of defense I would strongly recommend a method claim 2 restricted to both a purge gas volume corresponding to about the ratio of absolute desorption pressure to absolute product gas pressure and a phase longth of less than 3 minutes.

Please find enclosed a revised set of claims based on the proposal in your letter with the modifications outlined above. The new set of claims does not contain sub-claims corresponding to claim 6, 12, 14 and 16 forwarded with my letter of May 14, 1965, because you apparantly feel that these subclaims may be cancelled.

The new main method claim is clearly less distinguished over the Kahle patents than the previous one. The alterations compared to the versions proposed in your letter are to the best of my judgement necessary in order to not completely reduce our chances to obtain

valid protection. I.am, of course, prepared to file those claims you decide to file, but I wish to clearly warn that insisting on claims which are insufficiently restricted against the Mahle patents will probably affect our chances to convince the examiner of the level of invention. Since the present application will most probably be opposed after publication, any unsound argumentation now will facilitate the attack of the opponents and cause worse difficulties in the opposition precedure.

I can take care of the remaining objections of the examiner without additional information and will prepare a suitable response as soon as I have received your approval to the proposed claims. A request for an oral hearing will probably be rejected by the examiner (please compare the last paragraph of the Office Action of April 1, 1965) and in the present case would be of little help because the examiner concerned does not like interviews and tends to change his mind even after showing a positive opinion during a hearing.

Very truly yours,

Bnc.: set of claims

cc: Dr. C. Medrow with enclosure Dr. J.T. Tyson with enclosure

## DEFENDANTS' EXHIBIT W(6)

Pearlman Deposition of July 15, 1970, pp. 156-59, 176

ROBERT I. PEARLMAN, being first duly sworn according to law by the Notary Public, testified as follows:

DIRECT EXAMINATION BY MR. MCCORMICK:

Q Mr. Pearlman, will you please state your home address, and your age?

A 220 West Jersey Street, Elizabeth, Non Jersey, 07202.

I will be thirty-six in August.

Q What is your present position at Esso?

A I am a patent gounsel in the patent and licenses division.

Q That is Esso Research & Engineering?

A Correct.

Q You are an attorney, are you not?

A Yes.

Q Will you give me a rundown of your educational background?

A I spent two years at Columbia College and then two years in the engineering school at Columbia, ending up with a B. S. degree in chemical engineering. I then took a Master's degree in chemical engineering the next year, getting my Master's degree in 1956.

Q Was that all at Columbia?

A At Columbia.

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In New York City?

A yes. I then joined the patent department of Esso Research & Engineering Company and went to night law school, obtaining an LIB. degree from Fordham Law School in 1960.

Q That is as far as your graduate work was con-

A Correct.

Q You first entered the employ then of Esso in 1956, did you say?

A Correct.

Q Can you tell me what positions you have held with Esso?

A Well, when I joined the company I was, I think, termed a patent trainee. Probably that term applied until I had obtained my law degree. I don't recall exactly. And then I was titled a patent attorney or senior patent attorney. We have gone through several evolutions of titles and I get confused as to which applied when.

In 1961 I became a primary patent attorney, the term designating that you supervised a group of attorneys.

I left the company in September of 1962. When I returned in the rall of 1964 I had the title of patent associate.

In February of 1966, I believe, I was appointed patent counsel, which in effect was the term designating the principal attorney charged with given areas of the company's business

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and it included supervising attorneys so as to appropriately cover patents and licensing matters in those areas. Where were you during the period from September of 1962 until the fall of 1964? I was working for a patent law firm in New York City.

What firm was that?

Blum, Moskowitz, et cetera.

Will you explain for me the patent setup here at Esso Research? That is, do you have a patent department that is separate from contracts and licensing groups where one is responsible for prosecuting the application and the other handling licensing matters? Just describe it.

You are referring to the present organization?

Yes. Let us hear about the present time.

At the present time the patent and licensing group covers both patent prosecution and licensing in the subject areas of the company's business that they are concerned with.

An exception arises where the sale of technology is involved, where a technical sales division, another division of the company, has prime responsibility which it can delegate back to an attorney in the patent and licensing group.

In the particular case of heatless fractionation, that is in fact the way we operate. So that I have principal responsibility for the heatless fractionation field as a licensing project, even though it has been a sales project

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as opposed to acquisition.

Q Are you head of the patent and licensing group?

A No.

Q Who is the head?

A Rod Manahan.

Q Has this general arrangement held since about the beginning of 1960?

A No. We have gone through a variety of organizations.

Q Then in about 1960 was this responsibility split up?

A As I remember it, and I am now just using my recall, we had greater separation of prosecution activities as being handled by a patent division, whereas licensing activities were handled by group outside of the patent division.

Q Who headed the patent solicitation group in the area of 1957 to 1960?

A J. J. Small.

Q Who headed the contract and licensing section or group from 1960 onward?

A Well, as I recall, there were actually two groups that might be termed contract and licensing in the context that I believe you have phrased the question.

One was slanted toward petroleum processes and heavy technology.

Q That wouldn't be the group that we are interested

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A No, not that I recall.

Q Would you please, at the time of furnishing this other material that you have made notes of, please supply me a copy of the license dated June 1, 1959, with Gas Drying, Inc., and copies of all correspondence and memoranda in the rile to the time of termination? Again I understand that this is subject to privilege and that if you would hold anything for reasons of privilege that you will just give the dates and the sender and receiver. Is that correct?

MR. HEUTTMER: That is correct.

THE WITNESS: Yes, sir.

Q Mr. Pearlman, will you just take the time to go through the list of licensees and tell me whether anyone listed there has subsequently ceased to be a licensee, if you know?

A.E.I. Birlee

A Starting at Page 15 of the answer, D. D. Beirler
Company was merged with another licensee in Britain.

Q They are still a licensee, however?

A The license in effect was terminated and replaced by a new license.

Q I am primarily interested in the licensees in the United States.

A To expedite matters, I will restrict the answer to the United States licensees.

Applied Pneumatics as indicated was terminated in April